

CONDENSATE PURIFICATION

The Influence of Operating Conditions on
the Ion Exchange Processes



1	INTRODUCTION	<i>Page 2</i>
2	THE NEED FOR CONDENSATE PURIFICATION PLANT	<i>Page 2</i>
3	CONDITIONING CHEMICALS	<i>Page 2</i>
4	WATER QUALITY REQUIRED	<i>Page 3</i>
5	FACTORS AFFECTING THE PERFORMANCE OF CONDENSATE PURIFICATION PLANT	<i>Page 3</i>
	5.1 Flow Rate	<i>Page 4</i>
	5.2 Regeneration Procedures and Conditions	<i>Page 5</i>
	5.3 Composition of Water to be Treated	<i>Page 7</i>
	5.4 Mixed Bed - Cation Resin in Hydrogen Form	<i>Page 7</i>
	5.5 Mixed Bed - Cation Resin in Ammonium Form	<i>Page 8</i>
	5.6 Use of cation resin when treating amine dosed condensate	<i>Page 9</i>
	5.7 Filtration	<i>Page 10</i>
	5.8 Use of Powdered Ion Exchange Resins	<i>Page 10</i>
6	CONCLUDING COMMENTS	<i>Page 11</i>
	6.1 Purolite Performance information	<i>Page 12</i>
	Index	<i>Page 16</i>

1 INTRODUCTION

The term 'condensate purification' is normally applied to the treatment of condensed steam from turbines operating in the power industry. For once through boilers, both nuclear and fossil fuelled, or high heat flux boilers such as oil fired coastal stations, the whole of the condensate flow is likely to be treated in an additional plant to that used to provide the make-up water supply. Partial condensate purification facilities may be provided on large conventional coal fired plants, but in this case, the final stage of the make-up water treatment plant will be suitably sized to treat, typically, up to 25% of the feed flow to the boiler for short periods i.e., during start-up when contaminants in the system are most likely to be present.

In this publication, factors affecting the performance of full-flow condensate purification plant (CPP) are examined with particular attention to the functions of the ion exchange resins.

2 THE NEED FOR CONDENSATE PURIFICATION PLANT

Why is it necessary to treat condensate which may already be in a high state of purity? There are several reasons, but the most outstanding need arises from the fact that traces of soluble impurities present in the feed water entering a high pressure boiler can be concentrated within the system. The degree to which this occurs depends on the design of boiler, heat flux, oxide thickness at heat transfer surfaces, and the level of insoluble impurities. For example, concentration factors as high as 10^4 to 10^6 can arise at local sites within drum boilers: this means that $\mu\text{g}/\text{kg}$ quantities of impurities or even lower can concentrate up to mg kg^{-1} levels.

In a once-through type of boiler all the water entering a tube is evaporated in a single pass and salt concentration occurs at the water/steam transition point. The result of these concentration mechanisms is that there is a risk of corrosion of boiler tubes by ions such as chloride and sulphate, and if failures occur the economic penalties are very severe.

A special situation arises with once-through boilers operating under supercritical conditions, i.e. such that the critical pressure (221 bar) and temperature (374°C) is exceeded and a single phase fluid exists rather than two phase water/steam conditions. In this case, all the impurities in the boiler fluid will be present as the fluid enters the turbine. Consequently, there is a subsequent risk of substances depositing within the turbine. At the temperatures and pressures involved this includes metallic elements like copper and iron which have an appreciable solubility under the boiler conditions which reduces rapidly as the fluid passes through the high pressure section of the turbine

and can lead to the formation of hard, tenacious deposits, resulting in a deterioration in output from the turbine.

It follows that under these conditions the condensate purification plant has to be capable of removing copper and iron (soluble and insoluble species) to a very low concentration.

There are various potential sources of soluble contaminants into the water/steam circuits of power plants:

- **Cooling water from condenser in-leakage and this can be a particularly severe problem where sea water cooling is employed.**
- **Make-up water, this can arise from maloperation such that regeneration chemicals enter the system, the plant may over-run during the service cycle or complete removal of certain substances such as organic matter may not occur.**
- **The conditioning chemicals used to protect the circuit e.g. ammonia, morpholine and hydrazine can be regarded as sources of contamination if they are to be removed by the condensate purification plant.**

Insoluble impurities will usually be the corrosion products from the materials in the system. Copper and iron are the predominant species and hence they are usually included in the water quality specification. However, under commissioning conditions a number of other substances, in particular, silica from lagging and cementitious materials, may be present in insoluble form.

It follows from the foregoing that a condensate purification plant needs to be capable of removing both soluble and insoluble species to very low concentrations. Ion exchange resins can fulfil both requirements, but additional filtration, pre-coat or deep bed, have frequently been incorporated.

3 CONDITIONING CHEMICALS

Protection of the feed and boiler circuits in power plants employing condensate purification plant is provided by the addition of ammonia, to elevate the pH, and hydrazine, to remove any residual dissolved oxygen present.

The aim is to control pH between 8.8 - 9.6 with the actual pH being set by the particular site operating conditions. Normally a pH range of 8.8 to 9.2 will protect the system and minimize the transport of metallic impurities from the feed circuit to the boiler. However, should there be a risk of erosion/corrosion occurring it may be necessary to raise the pH to 9.4 or above. It should be noted that increasing the pH level can have a significant effect on the design and operation of CPP.

For example, the ammonia concentration has to be increased by a factor of 4 to raise the pH from 9.2 to 9.6. Consequently, this will increase the load on to cation sections of the plant by the same factor, thereby increasing the regeneration frequency.

Alternative volatile amines such as morpholine and AMP (2 amino - 2 methyl propanol) may afford better protection than ammonia, particularly where there is a risk of erosion/corrosion occurring. By providing improved pH conditions in the water phase of the two phase (steam/water) region of the boiler [1].

The use of these alternative amines will affect the operation and performance of the CPP designed to work under normal pH conditions using ammonia, as higher concentrations are needed than with NH₃, to achieve a given pH. Further details on the particular factors involved in operating CPP in this mode are given in Section 5.6.

The use of hydrazine generally poses no problems to the CPP. The breakdown products are mainly ammonia, from high temperature degradation, and nitrogen from the reaction with any oxygen in the water.

4 WATER QUALITY REQUIRED

Consideration of the quality of water required to be produced by CPP is closely related to developments that have occurred in CPP design over the years.

The original specification for water quality from CPP on super-critical fossil fuelled units was:

Conductivity 0.1 μ S/cm at 25°C
Sodium <5 μ g/kg

and with the advent of AGR nuclear stations this specification was used initially. However, investigational work had shown that the AGR **gas side** conditions at the boiler tube surfaces in the evaporator sections could give breakaway oxidation. To prevent this occurring operating procedures had to be changed, but this introduced an increased risk of corrosion occurring within the **water side** of tubes. It was realised that minute traces of acidic sulphates could be present in water from a CPP, particularly in the period immediately following a regeneration. Calculations were made on the concentration factors likely to arise in the boiler and these were used to indicate the quality of water required from the CPP to protect the system from pitting corrosion of ferritic steels and stress corrosion of austenitic materials. Accordingly, a more stringent water quality was set as follows:

Sodium 2 μ g/kg
Chloride 2 μ g/kg
Sulphate 2 μ g/kg
Conductivity <0.08 μ S/cm at 25°C

with the overall aim of achieving a balance of ions to provide neutral conditions at the heat transfer surfaces.

A similar standard was subsequently adopted for CPP on Super-critical and early gas cooled nuclear stations.

Meanwhile, operating experience was showing that PWR stations were suffering from corrosion due to the use of relatively poor quality water. High concentration factors of impurities occur in PWR steam generators, consequently the feed (CPP) quality needs to be compatible with these conditions. This has resulted in an even more stringent water specification being applied to the quality of treated water to be supplied to PWR plant as follows:

Conductivity	<0.06	μS/cm at 25°C
Chloride	<0.3	μg/kg
Sulphate	<0.5	μg/kg
Sodium	<0.3	μg/kg
Silica	<4	μg/kg

In addition to the above, low concentrations of iron and copper have to be maintained in the feed water to any high pressure power plant to minimise corrosion in the boiler and to prevent deposits in the turbine. Accordingly, a CPP has to be capable of producing water of very low iron and copper content.

The quality demanded will depend upon the specific type of plant to which the CPP is being applied. However, usually the standard required is that frequently specified for the feed water quality to H.P. boiler plant, i.e. total iron < 5 μ g/Kg: Total copper < 2 μ g/Kg.

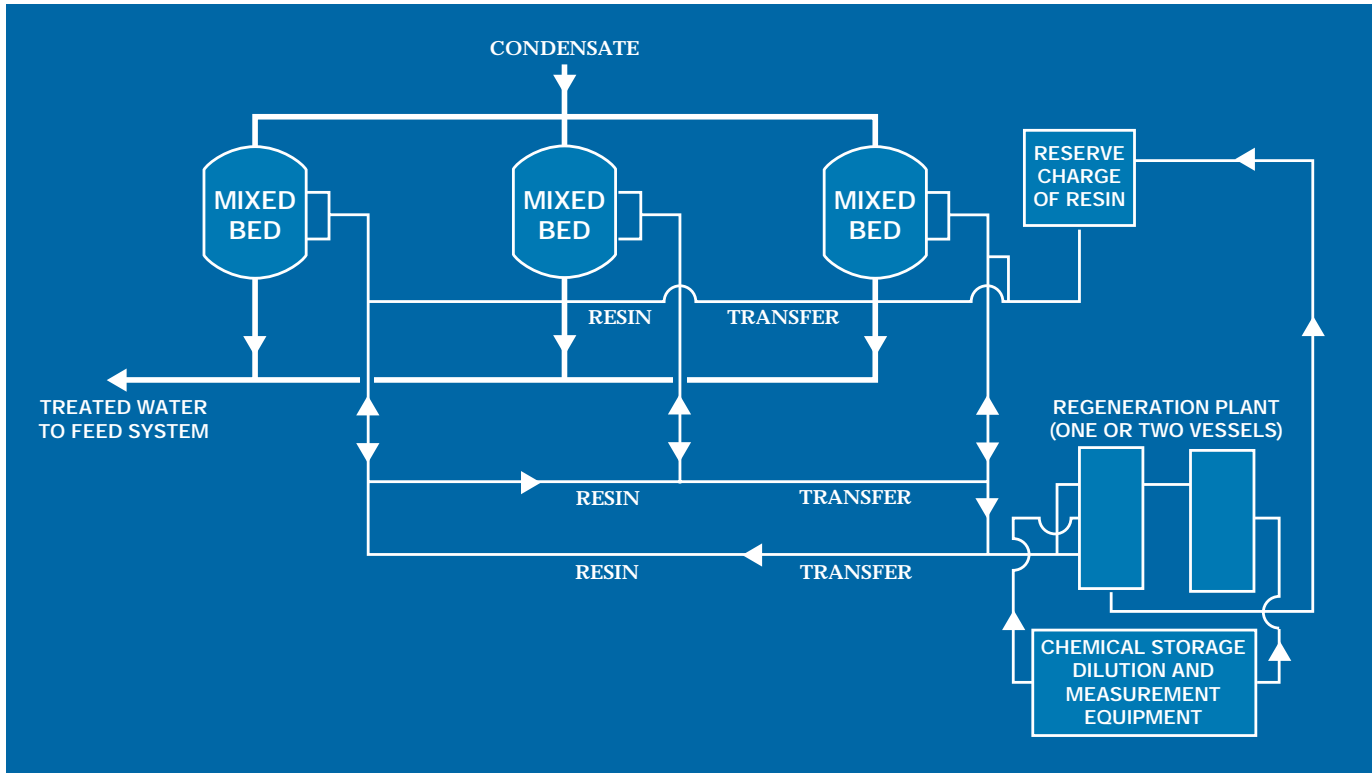
The combination of filtration and ion exchange capability within a CPP normally ensures that these limits are achievable.

It can be seen from the above that, progressively, a higher quality water has been demanded from CPP. The following sections will show how these requirements have affected the design and operation of CPP, and the choice of ion exchange resins.

5 FACTORS AFFECTING THE PERFORMANCE OF CONDENSATE PURIFICATION PLANT

A CPP has to produce the quantity of treated water required to the water quality specification at all times and this will include a variety of operating conditions. The ability of the plant to meet this requirement is dependent on both the design and operating conditions, and how these might affect the ion exchange process has to be a prime consideration. The performance and life of the ion exchange resins used might be affected,

Fig 1. Typical Condensate Purification Plant with Mixed Beds



consequently, the choice of resins needs to be closely related to the plant factors.

The main factors involved are:

- **Flow rate**
- **Regeneration procedures and conditions**
- **Composition of water to be treated**
- **Quality and quantity of treated water to be produced**

Fig.1 shows the layout of a typical CPP plant.

5.1 Flow Rate

A CPP has to be designed to filter and deionise large quantities of water. For a 660MW PWR unit, in the region of 1500m³/h of treated water has to be produced. Hence to minimise the capital cost of plant the ion exchange beds have to be operated at a high flow rate relative to normal ion exchange plant, and in the case of the mixed beds these are generally designed to operate at a specific flow rate of 100 - 150 m/h (m⁻³m⁻²h⁻¹)

High flow rates can result in two main effects:

- **Increased pressure drop, with a consequent increase in the risk of physical breakdown of resin.**
- **Decrease in the time for the Ion Exchange reactions to occur.**

By choosing particular types and particle sizes of resin, each of

these individual effects could be reduced in magnitude, but, unfortunately, in minimising one effect the other adverse effect might be accentuated. For example; pressure drop depends on flow rate and particle size, hence in using larger beads a lower pressure drop can be obtained. (The differential pressure is inversely proportional to the square of the particle size: therefore, if the particle size is doubled the differential pressure decreases by a factor of four!). However, the use of large beads proportionately decreases the surface area available for Ion Exchange and would result in slower kinetics and a consequent risk of obtaining a poorer quality water with reduced capacity.

Under normal condensate polishing conditions a high service flow rate alone is unlikely to result in a serious physical breakdown of the cation and anion resins. However, the resins can be weakened by other factors, such as the osmotic stresses that arise during regeneration, and high flow rate plus resin transfer are then additional factors that may lead to subsequent physical breakdown.

The major influence of a high flow rate is to decrease the time available for the ion exchange reactions to occur as condensate passes through a bed, and hence the kinetics of the ion exchange resins become more critical properties [7-13].

The overall rate of exchange is determined by a number of chemical and physical factors:

- diffusion of ions across the static film of water at the surface of a bead
- diffusion within a bead
- particle size of beads (surface area)
- exchange of ions onto the active groups of a resin
- types of ion present
- pH conditions within the bed.

For the highly ionised cation and anion resins used in CPP, the rate of exchange of ions within the active groups on the resin will be high, and the overall rate controlling factor will be the rate of diffusion across the static film of water at the surface of a bead. This always applies even when the resins are new. However, in service, deterioration in the performances of the resins may occur due to fouling and/or ageing. In this respect anion resins are more susceptible than cation resins. They are more likely to receive fouling species e.g. organic matter which could arise from a number of sources including sulphonates from the cation resin. Moreover, they are chemically less stable than cation types and some degradation of the strongly basic groupings will inevitably occur. It has been shown [10-14] that those effects result in poor anion exchange kinetics at the surfaces of the beads and thereby, the rate of exchange of ions at the surface then controls the overall rate of exchange.

The rate of exchange will differ for differing types of ions, but at the relatively low flow rates used in make-up water treatment plant such differences are rarely observed for **inorganic** ions. However, the difficulty encountered, on occasions, in satisfactorily removing **organic** species can at least be partially attributed to kinetic factors.

At the much higher flow rates used in modern CPP even the differences in the rates of exchange of **inorganic** ions become observable in practice. In particular, the sulphate exchange is slower than chloride exchange. The rate difference is of little practical significance when new resins are in use. However, as indicated above, deterioration in kinetics due to fouling/ageing occurs with time and results in an overall slower removal of these anions; furthermore, the low rate of uptake of sulphate relative to chloride ion is enhanced.

In recent years, a number of investigations on anion kinetics have been reported and fuller details relative to the above can be obtained from references [7-13]. The present position can be summarised as follows.

At the high flow rates used in mixed bed operations the anion resins are working near to the limits of their kinetic ability. The zone of exchange, which is the depth of bed required to produce the desired quality of water, is a significant proportion of the total bed depth. It follows that any deterioration, in service, of the kinetic ability will result in an increase in the length of the zone with two possible adverse effects.

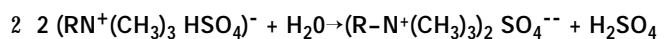
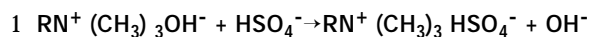
- The quality of water required may not be obtained.
 - The capacity of the resin for treating condensate contaminated with cooling water will be decreased.
- (See also Section 5.2 and 5.4)

5.2 Regeneration Procedures and Conditions

Regeneration of the ion exchange resins within the service vessels is not practicable owing to the wide variations in service and regeneration flow rates and the need to eliminate the risk of directly contaminating the water/steam circuit with the regeneration chemicals used (sulphuric acid or hydrochloric acid and sodium hydroxide). Consequently, in early CPP the resins were transferred from the service vessels to a single regenerator vessel, and the cation and anion resins were separated and regenerated in this vessel.

It is of vital importance that cross contamination of the resins by the wrong regenerant should be minimised hence the separation of the cation and anion resin components is a crucial stage in the regeneration procedure. Whilst the slight contamination of cation resin with sodium hydroxide when operating in the hydrogen form is undesirable, it is relatively unimportant when compared with contamination of the anion resin with sulphuric or hydrochloric acid which can result in difficulty in obtaining the required sulphate or chloride concentration in the treated water following regeneration.

The following equations illustrate how this arises (sulphuric acid regeneration).



Anion resin contacted by the sulphuric acid is converted to the bisulphate form (equation 1).

Subsequently when the resins are mixed and the final rinsing begins, the bisulphate form resin is converted into the sulphate form with the release of sulphuric acid (equation 2). This sulphate then has to be taken up by the bulk of the anion resin in hydroxyl form. With new anion resin this can be done, but it has been shown [2] that any deterioration in the kinetic performance of the anion resin due to fouling/ageing will result in the need for prolonged rinse periods before satisfactory sulphate concentrations can be obtained. The rate of uptake of sulphate ions by the anion resin is too slow so that there is not enough time for the sulphate released from a portion of the bed near to the bottom of the unit to be removed to the desired level before the water leaves the bed. The depth of this zone dictates the extent of the prolonged rinse requirement, and the depth will depend on the kinetic condition of the anion resin. For new resin a very short zone will exist, but this will increase progressively with any deterioration in the kinetic performance of the anion resin.

(Note that this problem can be partially ameliorated by allowing the mixed bed to stand for a period prior to return to service. However, this may not be possible on a short cycle designed plant or in the event of a severe condenser leak).

From the above it follows that the cation and anion resins need to be of suitable size and density to allow good separation to occur on backwashing.

A range of cation and anion resins combinations may be used and in general optimum separation will be achieved with cation resin of 0.7 - 1.2mm and anion resin of 0.42 - 0.85mm. The ideal effective particle sizes would be 0.8mm and 0.55mm for the cation and anion resins respectively.

Density differences are enhanced by using a gelular cation resin of high DVB (10%) and a macroporous anion resin, but there is a need to establish that this combination would be of adequate physical strength.

An inert material of intermediate density and particle size has been used to provide an additional buffer between the cation and anion resins and reduce resin cross contamination. Unfortunately on occasions difficulties have arisen due to the susceptibility of such materials to oils, greases and metal oxides: consequently they are unable to act consistently as satisfactory buffers in CPP.

Details of typical chemical and physical characteristics of a range of resins suitable for use in CPP mixed beds are given in Appendices 1-4.

In addition to using resins having optimum separation characteristics plant modifications have also been made to improve the regeneration process to reduce the risk of cross contamination arising, examples being:

Separate Cation - Anion Regeneration Units

One of the first modifications/improvements to condensate polishing regeneration systems was to employ, instead of a single regenerator, separate cation and anion regeneration units. Providing good separation could be achieved there was less chance of regenerant cross contamination and each regeneration unit could be specifically designed to give more freeboard for vigorous back-washing and air scouring. This is particularly important for a naked mixed bed which also acts as a filter. Originally the mixed bed resins were backwashed in the cation regenerator to separate the mixture into the two components.

Then via sluicing nozzles located at the resin interface in the cation regeneration/separation unit the anion resin was sluiced off the surface of the cation resin into its own regeneration unit.

While this system is used worldwide it has obvious limitations in

that it relies on the interface being always located at the exact position of the sluicing nozzles. This is not always possible to guarantee and hence excessive cross contamination can occur. Further improvements were obviously required.

CONESEP- NEI Thompson Kennicott [4]

Fig 2. The Conesep System

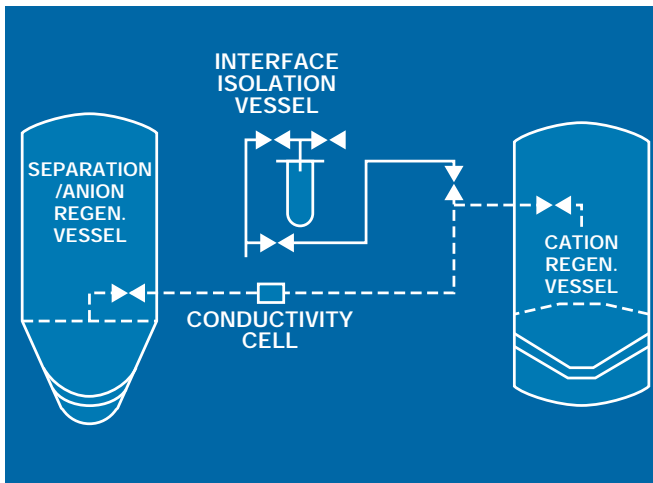


Fig 2 shows a diagram of plant.

The mixed bed is transferred from the service vessel to the main separation unit which also serves as the anion regeneration vessel. On backwashing, the resins separate and the lower cation resin layer is then hydraulically transferred to a separate vessel simply by introducing water into the base of the Conesep vessel and forcing resin to flow out through a transfer pipeline. During this transfer the anion/cation resin interface descends smoothly through the vessel, the base of which is cone-shaped to compress the interface, and eventually enters the transfer pipeline. In this pipe it is sensed by conductimetric or optical means and the transfer terminated. On the original full scale installation this procedure results in cation and anion cross contamination figures of about 0.3% v/v. [4].

The level of cross contamination is acceptable for plants aiming to produce water with sodium levels of less than 0.1 ppb when operating in H-OH mode.

Variations introduced since the design was first used include adjustments to the all important base design, the development of alternative interface sensing techniques and the development of a secondary separation stage. This involves a secondary classification, by backwashing, of the anion resin component after its regeneration with sodium hydroxide. This second separation relies on the fact that any cation resin beads in the anion resin are now in the more dense sodium form. Thus they are more easily separated from the anion resin which is now in the less dense OH form.

The small amount of cation resin recovered by this procedure is

moved to an interface isolation vessel and subsequently added to the next charge to be regenerated.

These improvements have particular benefit to operation in the ammonium or amine cycle when the cation resin in the mixed bed has to have a very low residual sodium content. Separation down to <0.06% v/v of cation resin in anion resin has been achieved on fullscale operating plant, [5].

TRIPOL- PWT Projects Ltd

In this type of plant the resins are not used as a mixed bed but are separated by screens into three layers cation - anion - cation [6] as shown in Fig 3. The resins are transferred from the service vessel for regeneration.

The cation and anion resins are kept apart in the regeneration system, even to the extent of having separate resin movement lines so that the cross contamination problem of the wrong regenerant on the resin is completely avoided. Resin ratios and volumes can be altered to suit particular operating conditions but typically the lead and trail cation are each 350mm deep, and the anion 500mm deep. The linear flow rate is typically 200m/h and the separated beds technique avoids the compaction which occurs in a deep mixed bed so that the headloss is about the same as a classic mixed bed condensate polishing plant running at 120m/h.

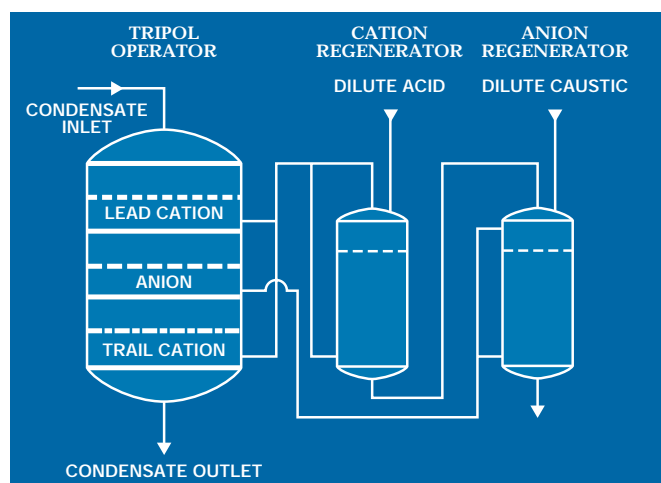


Fig 3. The Tripol Process

The process is not sensitive to resin type or indeed particle size. Both macroporous and gelular cation and anion resins have been used successfully although to achieve the best possible capacity under arduous conditions the usual recommendation is for a 10% DVB cation resin gel, and one of the modern high strength high capacity gel anion resins.

During the original development of the process it was observed that single beds of resins both cation and anion can exhibit better kinetics than occur in a mixed bed and these findings have been reported in detail [13]. Practically, this allows larger beads

of resin to be used without affecting the kinetics and also resulting in a lower headloss.

In the USA, two other processes are used to overcome cross contamination of the resins by the regenerant chemicals as follows:

AMMONEX - Crane Cochrane

The process was developed specifically for operating condensate purification plant with the cation resin of the mixed bed in ammonium form. Two regenerator vessels are used. Following transfer from the service vessels separation is carried out by back-washing. The anion portion is then transferred to the second regenerator and in this stage the resin transfer point is usually biased towards the anion section in order to limit the quantity of cation transferred with the anion resin. The anion resin is then regenerated with sodium hydroxide and rinsed. Ammonium hydroxide is then passed through the bed to convert any cation resin present from the sodium to ammonium form. Meanwhile the main cation section is regenerated with sulphuric acid and rinsed. The cation and anion resins are then mixed. Subsequently, the bed may be ammoniated either externally or during the service cycle.

SEPREX- Ecodyne Graver

In this system the resins are transferred from the service vessel to the first of two regeneration vessels. The resins are then separated by backwashing and the anion portion is transferred to the second vessel. After draining water from the anion resin, a 16% solution of sodium hydroxide is applied, this enhances the separation by floating the anion resin from any traces of cation resin that have been carried over. The anion resin is then taken from the vessel to the third vessel for rinsing. The cation resin remaining is rinsed and transferred to the main cation regeneration vessel for mixing with the next charge of cation resin to be regenerated.

The main cation bed is regenerated and rinsed in vessel one prior to the transferring to the third vessel for mixing with the anion resin in readiness for use.

5.3 Composition of Water to be Treated

As indicated in Section 3, the condensate to be treated can range in pH from 8.8 - 9.6 and this represents ammonia concentrations of up to 2.2mg/Kg NH₃ of water. In addition, in the event of a condenser leak salts from the cooling water, usually mainly chloride from sea water, will be present. Additionally, sulphate can be present in the mixed bed following a regeneration.

5.4 Mixed Bed - Cation Resin in Hydrogen Form

The majority of plants operate with the cation resin in hydrogen form and the end point of a service cycle, in the absence of condenser leakage, is a break through of ammonia, whether it be from a cation preceding a mixed bed or from a mixed bed working alone.

For a condensate of high pH the load on the cation resin is high and a resin is required which combines a high capacity for ammonia with a satisfactory resistance to attrition.

The capacity obtained will depend on:

- **The level of regeneration**
- **The breakpoint chosen**
- **The degree of cross linking of the resin (DVB content)**

Ammonium ion capacity determinations made on fullscale cation units have given a range of results from 0.7 -1.2 eq/l of resin. This range is at least partially due to the differing hydraulic conditions in large diameter beds giving variation in the uniformity of flow.

In the event of a condenser leak the loading onto the cation resin will increase due to the ingress of sodium, but the inherent capacity of the resin is not affected significantly and the run length to exhaustion can be estimated solely from the increased cation load.

From capacity considerations a standard 8% DVB gelular resin would be the preferred choice, but such a material is not sufficiently robust. An optimum choice would be the 10% DVB Purolite SGC100 x 10 gelular resin, which has high physical strength and a capacity for ammonia in the range of 1.2 -1.7 eq/l.

Usually, the removal of anions from condensate takes place solely within mixed beds. The exception is where a Tripol plant is installed and a separate anion section is present.

For a number of reasons, it is more difficult to predict the operating capacity of anion resin in CPP. In addition to factors such as the uniformity of flow conditions, the low concentration of anions to be removed and the high quality of product water required, anion resin kinetics will play a major role in determining both quality of water produced and the capacity for dealing with condenser leaks.

The deterioration of the kinetics of anion resin is likely to have the greatest influence on the capability of a bed for coping with condenser leaks. However, it must be emphasized that hydraulic factors such that non uniform uptake of ions occurs within the bed could have an over riding effect as the beds are shallow relative to the diameter of the vessels employed.

It is debatable whether in the short term, resins could be produced having superior kinetic properties which could be maintained for a longer period than the present products, and at present in some situations regular changing of the anion resin probably represents the best economic option. Nevertheless, efforts are being made continuously to improve the overall performances of anion resins.

The foregoing indicates that for CPP, as opposed to make-up water treatment plant, accurate operating capacity of the anion resins is difficult to specify. Historically, a figure representing 25% of the total volume capacity of the resin has been used in design calculations to estimate the time the bed could operate with a specific condenser leak. It is difficult to obtain accurate data on anion capacity from plant tests, but the indications are that even the 25% figure is increasingly difficult to achieve as the anion resin kinetics deteriorate. Capacities as low as 10-15% have been obtained under condenser leakage conditions on operating plants.

5.5 Mixed Bed - Cation Resin in Ammonium Form

Ammonium used to condition the water in feed and boiler systems represents the main load onto a cation resin operating in hydrogen form, and the higher the pH control level the greater the load. This is a disadvantage in that it leads to the need to regenerate the cation bed and or the mixed bed on a frequent basis. Regeneration of the mixed bed has attendant problems in relation to maintaining satisfactory sulphate levels.

By operating the cation resin in ammonium form, ammonia in the feed water is not removed, but adventitious cations such as sodium and calcium can be taken up by the resin. However, the difference in selectivity of ammonium and sodium ions is slight so that the sodium content of the resin has to be maintained at a very low concentration to obtain satisfactory low concentration of sodium in the treated water from the bed. The most suitable resin under these conditions is one which has a high selectivity for sodium relative to ammonium and has adequate physical properties. Available data indicate that selectivity differences with increased cross linking (DVB content) are slight therefore the choice can be made on the basis of satisfactory physical properties and cost. Purolite SGC100 x 10TL and Purolite C150TL are typical resins suitable for use under these conditions.

The capacity of cation resin in ammonium form depends upon the concentration of sodium present usually as the result of condenser leaks. The selectivity coefficient $K^{Na/NH_4} = 0.77$ is lower than $K^{Na/H} = 1.7$ hence the resin will have a lower capacity for sodium when operating in the ammonium form and more importantly the concentration of ammonium ion present results in the equilibrium leakage of sodium being high relative to hydrogen exchange. For example the concentration of sodium on the cation resin at the bottom of a bed cannot exceed 0.1% when treating a water pH 9.6 if a level of 2 $\mu\text{g}/\text{kg}$ sodium is to be obtained in the treated water. It follows that the capacity of ammonium form resin for sodium will be much lower than when operating in the hydrogen form. The equilibrium conditions for sodium/ammonium exchange lead to a longer exchange zone than for sodium/hydrogen exchange and hence a lower capacity. The actual capacity obtained will depend on the concentration present in the water being treated, the greater the concentration the greater the capacity.

In [15] figures are given of 7 eq m^{-3} at an inlet of $5 \mu\text{g/kg Na}$ and up to 150 eq m^{-3} at $350 \mu\text{g/kg Na}$ when treating condensate at pH 9.6 and working to a $2 \mu\text{g/kg Na}$ breakthrough point.

The pH conditions within a mixed bed operating with the cation in ammonium form will be those of the condensate i.e., 9.0 - 9.6. It has been shown that anion exchange rates are slower at these high pH's relative to hydrogen form cation operation [7]. The zone of exchange is extended and therefore a higher kinetic leakage of chloride and sulphate ions and a lower capacity would be predicted for the anion resin relative to when hydrogen form cation resin is used under comparable conditions. Nevertheless, data reported [15] on the performance of anion resin used in a Tripoli plant operating in the ammonium form, indicates that under high simulated condenser leak conditions a capacity equivalent to 30% of the total volume capacity of a macroporous anion resin was obtained. This in part may also reflect the better hydraulic conditions for anion exchange in such a plant relative to mixed beds.

5.6 Use of Cation Resins when Treating Amine Dosed Condensate

As mentioned in Section 3, amines other than ammonia may be used to protect nuclear systems from corrosion. To obtain the required pH conditions relatively high concentrations are needed i.e., at Oldbury Power Station in the U.K., morpholine levels in the range of 6-30 mg/kg have been used [1].

Experience with CPP plant treating condensate dosed with amines has shown that there is a risk of breakdown of macroporous cation resins [16] and that the degree of breakdown is dependent on the DVB content of the resin. The higher the DVB content the greater the risk of breakdown.

Laboratory tests showed that the breakdown arises from the osmotic forces present when an amine form resin is regenerated with acid, and that this effect is significantly enhanced by any contact between the resin and sodium hydroxide used to regenerate the anion resin. The tests showed that 20 and 25% DVB macroporous resins were particularly susceptible to breakdown, whereas 10% DVB gelular resin and 12% macroporous resin were virtually unaffected.

The following factors need to be considered in choosing the type of resin to be used when treating amines dosed condensate:

- **Physical stability**
- **Sodium/amine selectivity**
- **Resin separation (density/particle size)**
- **Capacity/acid requirement for regeneration**

We examine the following factors for several operating conditions.

H Form Operation

Under these conditions the physical strength and separation characteristics are likely to dictate the choice of resin. Selectivity differences between resins are slight and can be discounted. Both 10% gel or 12% macroporous cation resins could have satisfactory resistance to breakdown. However, the gel resin will also have enhanced separation characteristics due to its slightly higher density relative to a macroporous type. Additionally, it would also be expected to have a higher operating capacity.

Morpholine Form Operation

In this case, the presence of morpholine in the treated water affects the equilibrium leakage of sodium from the mixed bed. The leakage values depend on the selectivity coefficient $K_{\text{morpholine}}^{\text{Na}}$ of the cation resin and the sodium content of the resin.

Now the data in Ref 16 indicates that the selectivity coefficient increases with DVB content and hence to minimise sodium leakage a resin of the highest possible DVB content should be used. From selectivity considerations, therefore, a 20% DVB resin would be preferred when operating with morpholine. However, the risk of breakdown of this material is high and clearly outweighs its potential advantage on selectivity grounds.

If we then consider the 12% DVB resin which would have adequate strength we find that it has a much lower (factor of 20) selectivity coefficient than the 20% DVB material, and is only a factor of two higher than that of a 10% gel resin (which also has a satisfactory physical strength). It follows that there will not be an outstanding difference between the 10% gel and the 12% macroporous resin in terms of equilibrium leakage of sodium.

The sodium content of the resin is dictated by two main factors.

- **The quantity of cation present in the anion resin after separation which is subsequently in contact with sodium hydroxide.**
- **The level of sodium remaining on the separated cation resin after regeneration.**

Separation procedures such as described earlier should be capable of ensuring that a satisfactory low level of cation in anion resin is obtained in the absence of breakdown of cation resin.

However, if breakdown of the cation resin occurs with the production of small fragments of beads it could be then increasingly difficult to effect the required degree of separation. It follows that physical stability must be a prime consideration, and hence when choosing between a 10% DVB gel and 12% DVB macroporous resin a critical factor will be their relative resistance to physical breakdown.

This needs to be established in respect to products currently available. Additionally, individual batches of resin supplied for this application should be tested under simulated operating conditions.

2 Amino - 2 Methyl Propanol Form Operation

Similar conditions and considerations apply to those for morpholine form operation, but for AMP operation the selectivity coefficient [16] for the 12% DVB macroporous resin is a factor of 5 higher than the 10% gel resin. Hence, it is possible that a lower level of sodium leakage might be obtained with a 12% DVB macroporous resin, but the selectivity advantage might be partially affected by the greater difficulty in removing sodium from the 12% DVB resin during regeneration compared with the 10% material.

There is a need to establish the quality of water in terms of sodium leakage, likely to be obtained with these resins under conditions which accurately simulate plant conditions. This data together with that from the long term comparative physical stability tests mentioned in [16] should allow the correct type of cation resin to be chosen for operating under AMP form conditions.

5.7 Filtration

The water/steam circuit of power plant may be contaminated by insoluble corrosion products such as iron and copper. This occurs mainly during initial commissioning when concentrations of iron as high as 2000 $\mu\text{g}/\text{kg}$ can be experienced. Subsequent high levels of debris are likely to be present only during start-ups, when the system is disturbed. At this time concentrations of 100 - 200 $\mu\text{g}/\text{kg}$ may arise. During normal load operation total concentrations will usually be $<5 \mu\text{g}/\text{kg}$.

In older CPP, filters of various types were included prior to the ion exchange section. In subsequent designs, however, the ion exchange beds had also to act as filters. If a cation bed precedes the mixed bed this obviously acts as the main stage of filtration. In some cases, pre-coat filters are provided to operate either before or after the mixed bed unit.

A deep bed exchange unit acts as an efficient filter and depending on the inlet concentration of debris, 70 - 90% removal of debris is obtained. Particle size of the debris will dictate the degree of removal achieved. The debris can be satisfactorily removed from the bed by air scouring and backwashing.

There is no evidence that the type of resin used i.e., gelular or macroporous, affect the filtration efficiency.

5.8 Use of Powdered Ion Exchange Resins

Pre-coat filters have been adapted for use with powdered Ion Exchange resin. A thin film of powdered cation and anion resins is formed onto the outside of a hollow cylindrical element. A

variety of designs of elements exist but usually they comprise of filters wound onto a perforated stainless steel former. The liquid to be treated flows inwards passing through the ion exchange resin material and out to service.

When the resins are similar to those employed in deep bed ion exchange. The particle size of the resin is approx. 30 micron and when the cation and anion resins are mixed, a bulky floc forms. The characteristics of the floc vary depending on the ratio of cation/ anion resin used. To form the coat the mixed resin floc is passed on to the element and water is circulated until a satisfactory coat is obtained. The unit can then be put into service and operated until either a specified increase of pressure differential is reached or up to exhaustion of ion exchange capacity. The dry weight of the resins used to form the filter coat is equivalent to 1 kg per m^2 of element surface, and the usual service flow rate is 100 - 200 $\text{m}^{-2} \text{min}^{-1}$. The coat has a low resistance to flow, and typical pressure differentials are 0.1 - 0.2 bar for a freshly pre-coated unit. The unit can be operated to exhaustion of ion exchange capacity, or to a specified pressure differential (1.7 bar), if filtration is the main function.

When the end point is reached the spent resins are removed by passing a flow of water in the reverse direction to that employed during the service cycle.

The unit is then ready for recrating and the spent resins being of no further value are usually discarded.

The powdered cation resin can be supplied in hydrogen and ammonium forms, whilst the strongly basic anion resin is supplied in hydroxyl form. Additionally the Purolite Microlite powdered resins can be supplied already mixed in various cation/anion ratios, and in the required ionic form. This has a distinct advantage in the preparation of pre-coats. They can also be provided with a proportion of fibre.

Powdered resin systems have been used widely in the USA and Europe within condensate purification systems. In the USA they are used in conjunction with deep mixed beds and alone. However, their use alone is confined to stations where fresh water cooling is employed and in the event of a condenser leak, water of very low concentration relative to sea water enters the system. This highlights the limited ion exchange capacity of the process relative to conventional deep beds, and its main application is therefore likely to be as a polishing treatment after a deep bed or as a filter situated before a mixed bed.

Few powdered resin systems have been installed, for example in the UK at one power station such units are situated down stream of mixed beds, whilst in a sister station the units precede the mixed beds. At both installations the powdered resin units can be operated alone if required.

When installed after mixed beds, the main role of the units is to provide an additional ion exchange facility in the event of a premature breakthrough of the mixed beds, and to remove any residual soluble impurities present after the mixed bed stage. This could arise following the regeneration of a mixed bed, when sulphate concentrations in the treated water can be higher than in the middle of a service cycle. Under these conditions, the pre-coat units are capable of maintaining sulphate concentrations in the final treated water at $<0.2 \mu\text{g}/\text{kg SO}_4$ throughout the service cycle of a mixed bed.

Filtration may be the main function of a powdered resin system if the units are installed to precede the mixed beds. This is particularly useful during commissioning when high levels of debris may be present.

As might be expected, powdered resins have excellent filtration properties and even with high inlet debris levels the quality of the treated water can normally be maintained at <5 ppb. However, during periods when debris levels are high there will be a cost advantage in using cheaper filter media such as cellulose fibre. Such material can be used either along or in combination with the powdered ion exchange resin. The Purolite product Microlite FC is suitable for this application.

6 CONCLUDING COMMENTS

Three of the most frequently debated topics in respect to condensate purification are:-

- Whether to use mixed beds (or Tripol) alone or with a preceding cation unit.
- Whether to operate cation resin in ammonium, amine or hydrogen form.
- Types of resin which should be used.

It is useful at this point to consider the above from an ion exchange viewpoint.

Mixed Bed Versus Cation Unit- Mixed Bed

An additional cation unit will usually be considered only when the cation resins are to be operated in hydrogen form, and under these conditions the cation - mixed bed system is to be preferred from an ion - exchange function viewpoint.

The main advantages being:

- i) a higher quality water is produced.
- ii) a higher capacity can be obtained from the anion component of the mixed bed.
- iii) the system has a greater ability to cope with changes in the pH of condensate.
- iv) greater flexibility in the cation/anion ratio used in the mixed bed.

- v) by reducing the number of regenerations of the mixed beds, the potential mass of sulphate introduced into the system should be less.
- vi) an additional filtration facility is provided which may also provide some protection to the mixed bed resins.

Note that it could be argued that a Tripol plant is in effect operating with a preceding cation unit and that some of the above advantages may also be realised, notably (ii) (iii) and (vi).

Hydrogen Versus Ammonium or Amine Form Cation Resin in a Mixed Bed

The relative advantages of the two forms are:

Hydrogen Form

- Kinetic leakage of anions will be lower.
- Higher capacity under condenser leak conditions.
- Resin separation conditions may not be so critical as with ammonium form where superior regeneration facilities such as provided by Conesep Ammonex or Seprex are invariably required.
- Should be able to meet the more stringent water quality ($0.3 \mu\text{g}/\text{kg}$ sodium, chloride and $0.5 \mu\text{g}/\text{kg}$ sulphate) more easily.

Ammonium Form

- The number of regenerations of the mixed bed will be greatly reduced hence the risk of sulphate ingress into condensate will be lower.
- There is an obvious saving of both the condensate conditioning chemicals and the resin regenerants.

Amine Form

As for ammonium form, but a greater cost saving in the conditioning agent is achieved because a higher concentration of amine has been used to achieve a given pH relative to ammonia.

Types of Resin For C.P.P.

Ideally resins for C.P.P. should have the following qualities.

HIGH

- : resistance to osmotic shock and attrition (physical strength)
- : rates of reaction
- : cation: anion separation characteristics
- : capacities
- : resistance to fouling
- : thermal and oxidative stability
- : uniformity of physical size

LOW

- : resistance to flow (pressure loss)
- : organic leachables content

Over the years a variety of different types of resin have been used in CPP with varying degrees of success, frequently dictated by the plant operating conditions.

Resins have ranged from high DVB macroporous resins to low DVB gelular resins, whilst the combinations of cation/anion in mixed beds have ranged from gel: gel to macroporous: macroporous.

In recent years Purolite has concentrated on improving the physical strength of gelular resins to augment their advantage in respect to separation characteristics and capacity. The higher strength gelular cation resins are now commercially available and have been shown under certain operating conditions to have greater resistance to physical breakdown than high DVB content macroporous resins (5.6) Anion gelular resins of similar strength have also been developed and will shortly be commercially available.

Throughout this bulletin the author has attempted to illustrate how the performances of ion-exchange resins can be affected by a variety of operating conditions.

The examples provided are intended to show why the type of ion-exchange resin used often has to be a compromise between conflicting chemical and physical properties. The essential requirement is for the resin to produce the quality and quantity of water required at minimum operating cost.

6.1 Information Particular to the Performance of Purolite Ion Exchange Resins Recommended For Condensate Polishing is Given as Follows:

- i) Table 1 shows the Purolite products recommended for various operations and appendices 1-4 gives the properties of the individual resins.
- ii) A separate set of graphs is given in fig 5 and fig 6 illustrating resin separation and hydraulic pressure drop respectively against flow rate for various resin mixtures.
- iii) In relation to normal acid regeneration levels a schedule of capacities is given in fig 7.
- iv) Bearing in mind the rigorous physical demands on resins used in Condensate Polishing, Purolite realised some years ago that a relevant test was required in order to measure both the physical strength and the osmotic shock resistance of their resins in order to ensure that the useful life was predictably long.

After examination of the various methods available on an international basis it was decided that the method defined by Ball, Harries and Pickering [17] in their paper presented at the Pittsburgh Water Conference 1986 entitled "The Physical Strength of Ion Exchange resins" was one of the most rigorous and since it's

publicity has been shown to be the most practical when comparing test results with how resins actually behave in plant operation. Consequently Purolite installed this equipment both in their Quality Control and Technical Service Laboratories under licence from the Central Electricity Generating Board of the U.K. A simplified diagram of the apparatus is shown in Fig. 4

TABLE 1 PUROLITE RESINS FOR CONDENSATE POLISHING

UNIT OR SYSTEM		RECOMMENDED PUROLITE RESINS		
CATION UNIT		Purolite C150C or SGC100x10C		
MIXED BED (Including Conesep, Ammonex, Seprex)				
Cation	H:OH operation	Purolite C150TL or SGC100x10TL		
	NH ₄ :OH operation	Purolite C150TL or SGC100x10TL		
	Amine: OH operation	Purolite C150TL or SGC100x10TL		
Anion	H:OH operation	Purolite A500TL (or SGA400TL)		
	NH ₄ :OH operation	Purolite A500TL (or SGA400TL)		
	Amine:OH operation	Purolite A500TL (of SGA400TL)		
TRIPOL				
Cation	H:OH	Purolite SGC100x10TL		
	NH ₄ :OH	Purolite SGC100x10TL		
	Amine:OH	Purolite SGC100x10TL		
Anion	H:OH	Purolite SGA400CL		
	NH ₄ :OH	Purolite SGA400CL		
	Amine:OH	Purolite SGA400CL		
PRE-COAT FILTERS				
Cation	H:OH	Microlite PrCH		
	NH ₄ :OH	Microlite PrCN		
Anion	H:OH	Microlite PrAOH		
	NH ₄ :OH	Microlite PrAOH		
	Filter Fibre	Microlite FC		
Specific Mixtures of above are:				
		RATIOS		
		C/A		
MB 1 to 1H	Acid/Base	H ⁺ /OH ⁻	1/1	
MB 1 to 1N	Acid/Base	NH ₄ ⁺ /OH ⁻	1/1	
MB 2 to 1H	Acid/Base	H ⁺ /OH ⁻	2/1	
MB 2 to 1N	Acid/Base	NH ₄ ⁺ /OH ⁻	2/1	
MB 3 to 1H	Acid/Base	H ⁺ /OH ⁻	3/1	
MB 3 to 1N	Acid/Base	NH ₄ ⁺ /OH ⁻	3/1	
MB 3 to 2H	Acid/Base	H ⁺ /OH ⁻	3/2	
MB 3 to 2N	Acid/Base	NH ₄ ⁺ /OH ⁻	3/2	
		RATIOS		
		F/R	C/A	
OG-4H	Acid/Base	H ⁺ /OH ⁻	1:1	1:1
OG-4N	Acid/Base	NH ₄ ⁺ /OH ⁻	1:1	1:1
OG-6N	Acid/Base	NH ₄ ⁺ /OH ⁻	2:1	2:1
OG-7H	Acid/Base	H ⁺ /OH ⁻	1:2	3:1
OG-12H	Acid/Base	H ⁺ /OH ⁻	1:2	4:5
OG-12N	Acid/Base	NH ₄ ⁺ /OH ⁻	1:2	4:5

Essentially "categorised" resin samples are subjected to cycling with either acid (cation resin) or alkali (anion resin) with alternative treatment with sodium chloride. After each chemical cycle the resin is hydraulically pumped against a top screen in the attrition tube and allowed to drain back down to be ready for the next chemical cycle.

Percent resin breakdown is then assessed after a certain number of cycles depending upon the generic category of resin under test.

Table 2 shows breakdown percentage criteria that Purolite follows in the manufacture of their various products.

TABLE 2

	Standard gel		Supergel		Macroporus	
	C100 x 10	A 400	SGC100x10	SGA400	C150	A500
No of cycles	25	25	100	100	500	500
% Breakdown*	< 10	< 20	< 10	< 10	< 5	< 5

* As defined in test method by reduction in mean diameter.

Fig 4. O.S.A. Test Apparatus

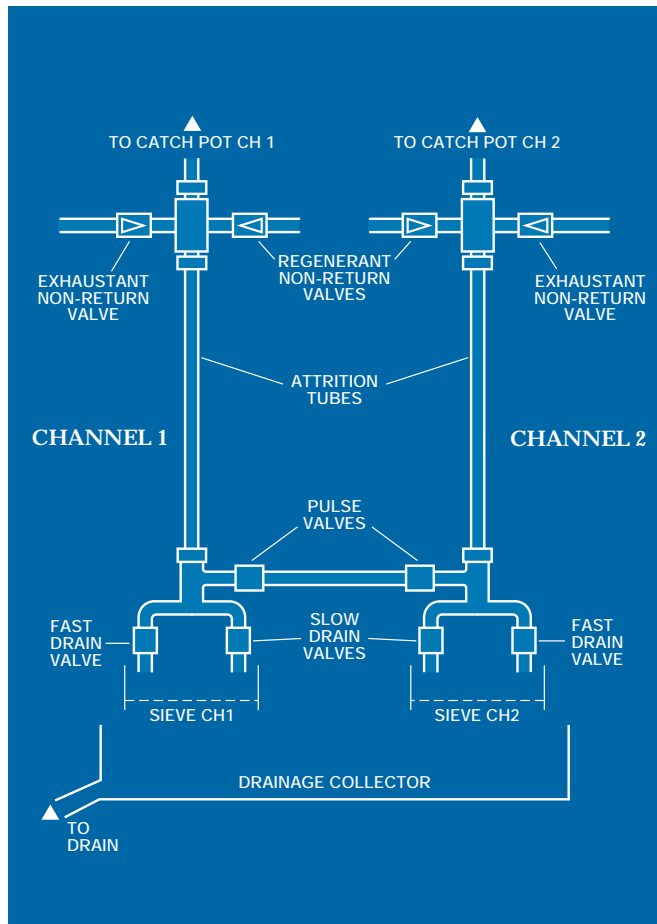
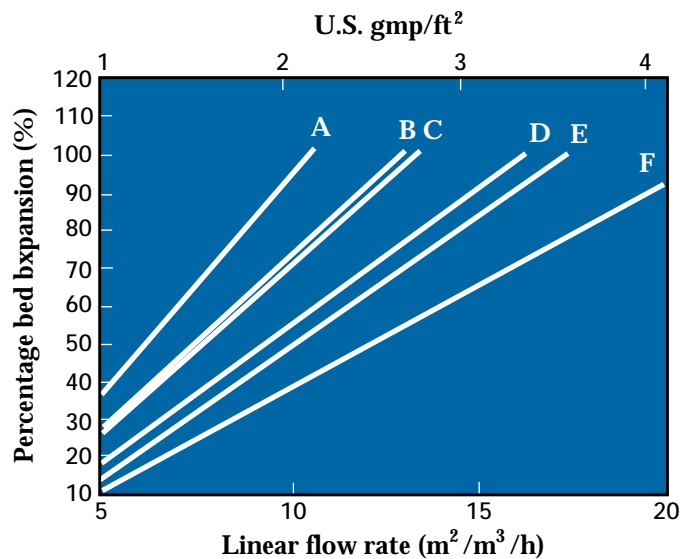


Fig 5. Backwash - Resin Separation

The figure below indicates backwash characteristics for a Purolite macroporous TL grade combination. For good separation of the bed 100% expansion is required. At below 80% expansion poor separation is likely.



- A = 1 : 2 Cation - Anion ratio 20°C
- B = 1 : 2 Cation - Anion ratio 30°C
- C = 1 : 1 Cation - Anion ratio 20°C
- D = 1 : 1 Cation - Anion ratio 30°C
- E = 2 : 1 Cation - Anion ratio 20°C
- F = 2 : 1 Cation - Anion ratio 30°C

For gel resin combinations allow 5-10% increased flow rate for same bed expansion.

Fig 6. Pressure Drop

The figure below indicates pressure drop across Purolite TL grade resins at Condensate Polishing Plant linear flow rates when clean. During plant operation the filtration of suspended material and bed compaction will lead to increased pressure loss. It is recommended that a margin of greater than 50% is allowed in plant design. The exact pressure drop across the ion exchange bed will be dependent on condensate temperature, crud loading and cycle length (bed compaction).

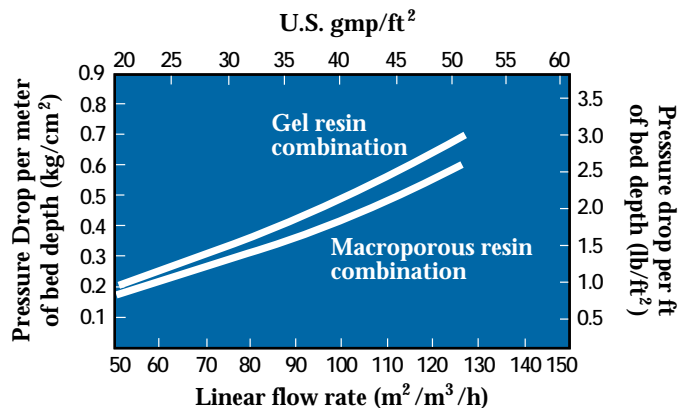
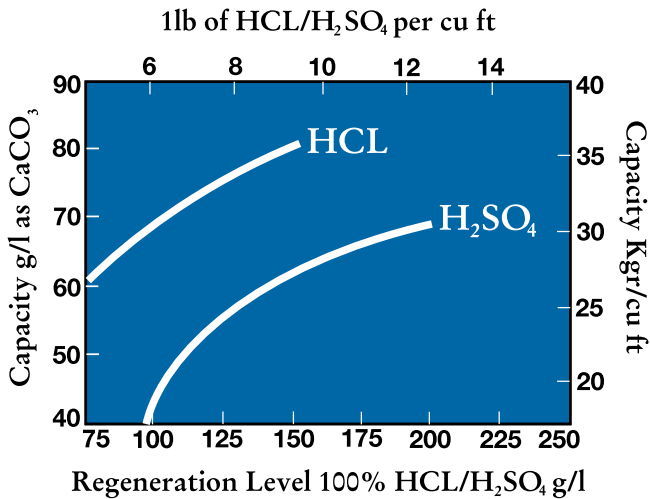
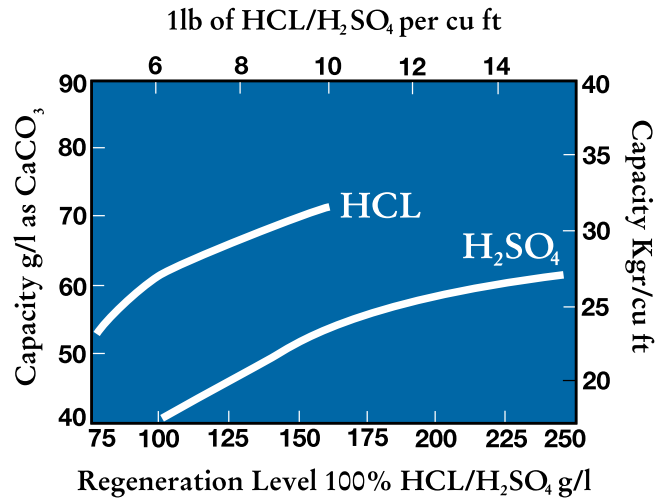


Fig 7. Cation Resin Capacities

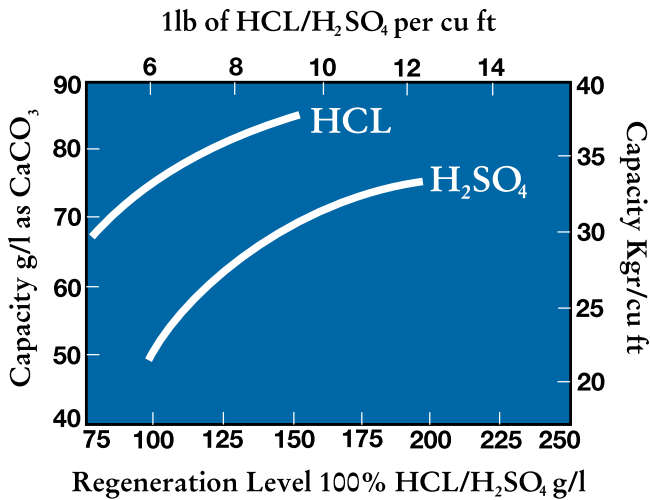
**Hydrogen Cycle Operation
Purolite SGC-100x10TL**



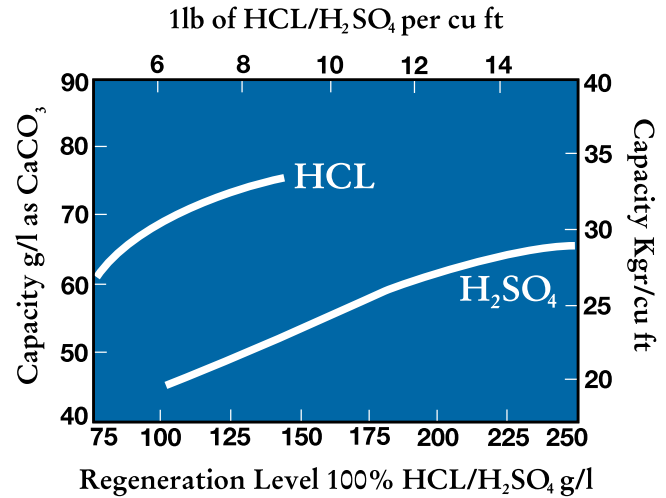
**Hydrogen Cycle Operation
Purolite C-150TL**



**Ammonia Cycle Operation
Purolite SGC-100x10TL**



**Ammonia Cycle Operation
Purolite C-150TL**



The above capacities are based on dosed condensates.

PUROLITE SGC-100x10TL

(Clear Gel Strong Acid Cation Exchange Resin)

Typical Chemical & Physical Characteristics

Polymer Matrix Structure	Gel Styrene- divinylbenzene
Physical Form and Appearance	Clear amber spheres
Whole Bead Count	>95%
Functional Groups	Polystyrene Sulphonate
Ionic Form (as shipped)	H ⁺ form
Shipping Weight g/l (lb/ft ³)	820 (51)
Particle Size Range	+1.2mm <5% -0.71mm <1%
Effective Size	0.8mm
Uniformity Coefficient	1.25 max
Moisture Retention H ⁺ form (Na ⁺ form)	47-50% (40-43%)
Reversible Swelling (Na ⁺ →H ⁺)	5% max
(NH ₄ ⁺ →H ⁺)	4% max
Secific Gravity Moist H ⁺ Form (Moist Na ⁺ Form)	1.20 (1.29)
Total Exchange Capacity Na ⁺ form (wet volumetric)	2.0 meq/ml min
(dry weight)	4.4 meq/g min
Maximum Operating Temperature °C (°F), Na ⁺ form	140 (285)
H ⁺ form	120 (250)
pH Range	No limitations

PUROLITE SGA-400TL

(Clear Gel Type 1 Strong-Base Anion Exchange Resin)

Typical Chemical & Physical Characteristics

Polymer Matrix Structure	Gel Styrene- divinylbenzene
Physical Form and Appearance	Clear golden pheres
Whole Bead Count	>95%
Functional Groups	Type 1 Quaternary Ammonium
Ionic Form (as shipped)	SO ₄ ⁻ form
Shipping Weight g/l (lb/ft ³)	690 (43)
Particle Size Range	+ 0.85 <5% -0.42mm <1%
Effective Size	0.55mm
Uniformity Coefficient	1.35 max
Moisture Retention CL ⁻ form	48-54%
Reversible Swelling (CL ⁻ →OH ⁻ max)	20%
Specific Gravity CL ⁻ Form	1.08
Total Exchange Capacity CL ⁻ form (wet volumetric)	>1.3 eq/l min
(dry weight)	>3.7 eq/kg min
Max Operating Temperature °C (°F) CL ⁻ Form	100 (212)
OH ⁻ Form	60 (140)
pH Range (Stability)	0-14

PUROLITE C-150TL

(Macroporous Strong Acid Cation-Exchange Resin)

Typical Chemical & Physical Characteristics

Polymer Matrix Structure	Macroporous Styrene- divinylbenzene
Physical Form and Appearance	Pale-brown opaque spheres
Whole Bead Count	>95%
Functional Groups	Polystyrene Sulphonate
Ionic Form (as shipped)	H ⁺ form
Shipping Weight g/l (lb/ft ³)	760 (47.5)
Particle Size Range	+1.2mm <5% -0.71mm >1%
Effective Size	0.8mm
Uniformity Coefficient	1.25 max
Moisture Retention H ⁺ form (Na ⁺ form)	54-59% (48-53%)
Reversible Swelling (Na ⁺ →H ⁺)	5% max
(NH ₄ ⁺ →H ⁺)	4% max
Specific Gravity Moist H ⁺ Form (Moist Na ⁺ Form)	1.18 (1.25)
Total Exchange Capacity Na ⁺ form (wet volumetric)	1.8 meq/ml min
(dry weight)	4.4 meq/g min
Maximum Operating Temperature °C (°F) Na ⁺ form	140 (285)
H ⁺ form	120 (250)
pH Range	No limitations

PUROLITE A-500TL

(Macroporous Type 1 Strong-Base Anion Exchange Resin)

Typical Chemical & Physical Characteristics

Polymer Matrix Structure	Macroporous Styrene- divinylbenzene
Physical Form and Appearance	Pale-brown opaque spheres
Whole Bead Count	>95%
Functional Groups	Type 1 Quaternary Ammonium
Ionic Form (as shipped)	SO ₄ ⁻ form
Shipping Weight g/l (lb/ft ³)	680 (42.5)
Particle Size Range	+ 0.85 <5% -0.42mm <1%
Effective Size	0.55mm
Uniformity Coefficient	1.35 max
Moisture Retention CL ⁻ form	53-58%
Reversible Swelling (CL ⁻ →OH ⁻ max)	10%
Specific Gravity, Moist CL ⁻ Form	1.07
Total Exchange Capacity CL ⁻ form (wet volumetric)	>1.5 eq/l min
(dry weight)	>3.7 meq/g min
Max Operating Temperature °C (°F) CL ⁻ Form	100 (212)
OH ⁻ Form	60 (140)
pH Range (Stability)	0-14

INDEX

Subject	Page
AGR power stations	3
2 Amino - 2 methyl propanol	3, 10, 11
Ammonex	7, 11
Ammonia addition	2, 3, 7, 8, 11
Attrition (resistance to)	8, 11, 12, 13
Bisulphate	5
Boilers - once through	2, 3
Boiler tubes - Corrosion of	2, 3
Cation - Anion resin separation	5
Chloride Ion Exchange	5, 11
Concentration Factors	2, 3
Condenser leakage	2, 7, 8, 9, 10
Conesep	6, 11
Contamination of Condensate	2, 6
Copper	2, 3, 10
Cross Contamination (of resin with regenerant)	5
Crud	3, 6, 10, 11, 13
D.V.B. content of Cation resin	6, 7, 8, 9, 10, 12
Filtration efficiency	10
Flow rates	4
Fouling and ageing of I.E.R.	5
Heat transfer surfaces	4
Hydrazine addition	2, 3
Interface isolation vessel	6
Iron	2, 3, 6
Inert 'spacer' resin	6
Kinetics	4, 5, 7, 8
Microlite	10
Mixed beds	4
Morphaline	3, 9, 11
Osmotic shock	4, 9, 12, 13
pH of condensate	2, 3, 8, 11
Pre-coat filtration	2, 10, 11
Pressure Drop	4, 10, 13
PWR power stations	3
Resin separation - degree of	7, 8
Selectivity coefficient	8, 9
Seprex	7, 11
Sodium leakage	3, 5, 6, 7, 8, 9, 11
Start up	10
Sulphate ion exchange	5, 11
Sulphonates	5
Treated condensate specifications	3
Tripol	7, 11, 12
Zone of exchange	5

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