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Condensate Polishing Performance Assessment: Use of Separate Bed Single Vessel Designs

Condensate Polishing Performance Assessment: Use of Separate Bed Single Vessel Designs

1014130

Final Report, February 2008

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This report describes research sponsored by the Electric Power Research Institute (EPRI).

The report is a corporate document that should be cited in the literature in the following manner:

Condensate Polishing Performance Assessment: Use of Separate Bed Single Vessel Designs.
EPRI, Palo Alto, CA: 2008. 1014130.

PRODUCT DESCRIPTION

EPRI guidelines recommend the use of condensate polishing in fossil power stations to provide on-going protection against the ingress of impurities and thus minimize corrosion and deposition problems that could otherwise occur in steam/water cycles. The most commonly used types of polishing plants rely on the use of mixed beds of cation and anion exchange resins. Unfortunately, although the effectiveness of properly designed and operated mixed bed polishers is well established, their use can require a significant level of attention and effort. Given the current demand to reduce all operational costs, there is interest in methods of condensate polishing that require less manpower and that can easily be used in the economical ammonium form. One such alternative, separate beds or layers of anion and cation resins, is widely used in water treatment plants; but the approach has not been generally regarded as capable of yielding the polished condensate qualities required in power plants. Over the last twenty years techniques of using separate bed condensate polishing have developed, however; and this report reviews the designs used and their applicability to modern fossil power stations.

Results and Findings

In comparison to the large number of mixed bed condensate polishing plants in use, separate bed plants are less commonly employed. They are in use or have been in use in Australia, Denmark, Holland, Germany, New Zealand, Singapore, and South Africa. These systems can be broadly divided into plants using separate deep beds of resins in separate vessels and plants employing a proprietary approach of shallow layers of cation and anion resins contained in one vessel. There is clear evidence that they are capable of yielding polished condensates with cation conductivities of < 0.1 µS/cm, with some claimed to be as low as 0.06 µS/cm. Levels of sodium, chloride, and sulfate are reported to be < 1 µg/kg (ppb) when operating either in the H-OH mode or in the ammonium form at high pH. Some stations report even lower leakage levels. Stations operating separate bed polishers in the ammonium form claim a greater ease of use relative to the effort involved in using mixed beds in this mode. The cost of a separate bed polisher that uses separate vessels will probably be significantly higher than that of a conventional mixed bed plant, but the cost of proprietary layered beds in a single vessel design should be very similar to conventional mixed bed systems.

Challenges and Objectives

The use of condensate polishing by fossil power stations is still not completely accepted despite EPRI's work showing their overall financial benefit and other advantages. The cost and perceived manpower requirements of polishing inhibit its adoption by some utilities. Separate bed plants answer some of these objections. The evidence given in this report shows that separate bed polishers are simpler to use than mixed bed units, yield a quality of condensate that meets fossil power station requirements, and facilitate operation in the economical ammonium form that markedly reduces the quantity of chemical waste derived from the regeneration processes.

This report will be of interest to designers, station management, station chemical specialists, and to those interested in the environmental impact of the operation of power stations.

Applications, Values, and Use

The adoption of separate bed polishers offers a simpler form of condensate polishing and one that could be used by stations that operate without the aid of specialist chemical staff. When operating in the ammonium form and in the absence of condenser leaks or frequent start-ups, service runs of 4-6 weeks should be attained without making the subsequent resin regeneration procedures difficult. Separate bed polishers are in successful use on conventional drum boiler units, once-through units, ultra super critical units, and on at least one combined cycle gas turbine station.

EPRI Perspective

EPRI has consistently supported the use of condensate polishing in all types of fossil power stations but understands the growing need to make such processes simpler, more robust, and less demanding of manpower. EPRI also recognizes the benefits of operating polishers in the ammonium form on those stations that can usefully employ the technique. Separate bed condensate polishing offers a way of achieving some or all of these objectives, although the capital costs involved are not likely to be lower than those of conventional mixed bed plants. The behavior of mixed bed polishers has, over the years, been scrutinized in great detail. That of separate bed polishers has not received the same levels of study except for some very useful trials of prototype layered separate bed plants. Notably, power stations in Australia have adopted the approach and experienced many years of satisfactory operation. Ideally, further and more detailed information on the behavior of separate bed polishers on modern power stations would be desirable, particularly in regards to their performance in the face of severe challenges such as large condenser leaks.

Approach

The project team studied the performance of separate bed condensate polishing plants in comparison with conventional mixed bed plants. Separate bed polishing plants, although not widely employed, are used in a number of countries; this real-world experience was the main basis for the assessments in this review. The team derived further information from published work describing tests carried out on prototype separate bed polishers in the 1980s, including tests performed by Southern California Edison on EPRI's behalf.

Keywords

Condensate polisher
Ion Exchange
Resin
Separate beds
Tripol
Cycle chemistry

ABSTRACT

As part of its on-going effort to maximize the availability of fossil power plants, EPRI has encouraged the adoption of condensate polishing. However, some power stations are concerned about the manpower requirements of many of the types of polishers currently employed, most of which are based on the use of mixed beds of anion and cation resins. They would welcome a design that is simpler to use. In this regard, EPRI recognizes that separate bed polishing may have benefits in terms of ease of use both in the conventional H-OH mode and in the economical ammonium mode and initiated the review of separate bed systems described in this report. The review shows that two general approaches to separate bed polishing are currently in use: separate beds in separate vessels and a proprietary design employing layers of cation, anion, and cation resin in a single vessel. Variants of the separate beds in separate vessel approach include plants using in-situ regeneration, counter flow in-situ regeneration, and those relying simply on a cation bed followed by an anion resin bed.

Although few if any problems have been reported by power plants using separate bed polishing, there is not a great deal of detailed information available in the literature when compared with the wealth of information available on the use of mixed beds in high purity water situations. EPRI members in Australia and New Zealand have provided very useful information on their experience with separate bed polishing for this report, which also includes information on prototype trials of the layered separate bed design. The most searching of these prototype trials was sponsored by EPRI and carried out by Southern California Edison in the early 1980s. That study concluded that the design was suitable for use on fossil power stations but would not meet the condensate quality demands of nuclear power stations. There is also evidence from plant experience at two utilities that an acceptable quality of condensate can be obtained from two-stage systems using only cation exchange followed by anion exchange. This finding offers the possibility of simplifying the approach of using layered beds in a single vessel. These and other aspects of the use and operation of separate bed polishers need to be explored further.

The investigators conclude that polishing plants based on the use of separate beds or layers of anion and cation resins can, in the absence of serious contamination, consistently yield condensate with impurity levels that comfortably meet EPRI targets. Based on power station reports, such systems are probably easier to operate than mixed bed units and certainly facilitate the use of ammonium form operation. It would, however, be interesting to study their behavior in the face of very serious condenser leaks and to compare it with the behavior predicted for conventional mixed beds.

ACKNOWLEDGEMENTS

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These contributions are gratefully acknowledged.

CONTENTS

_1_ BACKGROUND TO THE USE OF SEPARATE BEDS IN CONDENSATE POLISHING......1-1

1.1 EPRI Interest in the Application of Separate Bed Condensate Polishing on Fossil Power Stations 1-1

1.2 The Use of Separate Beds of Resins in Separate Service Vessels of a Conventional Design 1-2

1.2.1 An Early Design Proposal 1-2

1.2.2 Studies at KEMA 1-2

1.2.3 Power Station Experience in The Use of Separate Beds/Separate Vessels in Condensate Polishing 1-2

1.2.3.1 German Power Stations 1-2

1.2.3.2 Danish Power Stations 1-5

1.2.3.3 South African Power Stations 1-6

1.3 The Tripol^R System 1-7

1.3.1 Development of the Process 1-7

1.3.1.1 Preliminary Studies Using Small Scale Separate Columns 1-7

1.3.1.2 Pilot Plant Tests 1-8

1.3.2 Use of Tripol^R on Power Stations 1-9

1.3.2.1 Power Stations Using Tripol^R 1-9

1.3.2.2 Callide C Power Station, Australia 1-9

1.3.2.3 Loy Yang B Power Station, Australia 1-11

1.3.2.4 Stanwell Power Station, Australia 1-11

1.3.2.5 Tarong North, Australia 1-14

1.3.2.6 Huntly e3p Project, New Zealand 1-15

1.4 References 1-15

_2_ DISCUSSION OF POLISHING AND THE ROLE OF SEPARATE BEDS IN FOSSIL PLANTS 2-1

2.1 Deep Separate Condensate Polishing Plants 2-1

2.2 Design and Operation of Tripol^R Polishing Plants 2-2

2.3 Separate Beds and Ammonium Form Operation 2-3
2.4 Regeneration of Separate Bed Resins 2-4
2.5 Applicability of Separate Bed Condensate Polishers 2-5
2.6 Suggested Further Work 2-6
    2.6.1 Collate and Share Operating Experience 2-6
    2.6.2 Ability of Separate Bed Polishers to Treat Very Large Condenser Leaks 2-7
    2.6.3 Post Regeneration Resin Purification 2-7
    2.6.4 Two Stage Separate Bed Polishing Plant Designs 2-9
2.7 Conclusions 2-9
2.8 References 2-10

A STUDIES OF THE TRIPOL^{R} CONDENSATE POLISHING SYSTEM A-1
A.1 Pilot Plant Tests at Gladstone Power Station, Australia A-1
A.2 Pilot Plant Tests at Vales Point Power Station, Australia A-1
A.3 Pilot Plant Tests Drakelow Power Station, CEGB, UK A-1
A.4 EPRI Sponsored Pilot Plant Tests of the Proprietary Tripol^{R} Layered Separate Bed Condensate Polishing System by Southern California Edison, USA A-6
    A.4.1 Introduction and Background A-6
    A.4.2 Experimental Program and Results A-6
    A.4.3 Resin Studies Employing Weak Acid Cation Resins as an Aid to Understanding Leakage of Sulfate from Strong Acid Cation Resins as Seen On the Prototype Tripol^{R} Polisher A-12
    A.4.4 Summary and Conclusions of Tests of Prototype Tripol^{R} Condensate Polishing System by SCE A-14
A.5 Field Operating Experience: The Behaviour of a Tripol^{R} Condensate Polishing Plant at Callide C Power Station, Australia During a Large Condenser Leak A-16
A.6 Miscellaneous Additional Information On Strong Acid Cation Resin and Sulfate Leakage A-19
    A.6.1 Effect of Bead Size A-19
    A.6.2 Sulfate Contribution from Corrosion Debris A-19
    A.6.3 Effect of the Fouling of Cation Resins with Anion Resin Fines and Quarternary Amines A-20
    A.6.4 Oil Fouling of Resins A-20
A.7 References A-21

LIST OF FIGURES

Figure 1-1 Design of Mannheim Deep Cation-Mixed Bed Polishing Plant, 1968 1-3

Figure 1-2 Design of Mannheim Deep Mixed Bed Condensate Polishing Plant, 1972 1-4

Figure 1-3 Design of Mannheim Deep Separate Bed Condensate Polishing Plant, 1997 1-4

Figure 1-4 Three Valve Arrangement on Regenerant Lines to Separate Bed Polishers Using In-Situ Regeneration 1-5

Figure 1-5 Diagram of Prototype Tripol[R] Test Facility Used In SCE/EPRI Trials 1-9

Figure 1-6 Tripol[R] Vessel Used at Stanwell Power Station, Queensland Australia 1-14

Figure A-1 Tripol[R] Condensate Polishing Plant Layout, Renouf and Smith. 1981 .... A-3

Figure A-2 Hydrogen Form Operation of Tripol to Ammonia Breakthrough at pH 9.6 Using Gel Cation and Anion Resins and Operating On a Condensate Without Simulated Condenser Leaks. Source, Ion Exchange Technology, D. Naden and M. Streat, Ellis Horwood, 1984 .... A-4

Figure A-3 Ammonium Form Operation of Tripol at pH 9.6 With Simulated Condenser Leak (500 ppb Sodium) A-5

Figure A-4 Sodium Levels in Condensate at Stages Through the SCE Prototype Tripol Vessel Operating in the H-OH Mode A-9

Figure A-5 Chloride Levels in Condensate at Stages Through the SCE Prototype Tripol[R] Vessel Operating in the H-OH Mode A-10

Figure A-6 Sulfate Levels in Condensate at Stages Through the SCE Prototype Tripol[R] Vessel Operating in the H-OH Mode. A-11

Figure A-7 Conductivity of Inlet Condensate and Polished Water During a Condenser Leak at Callide C Power Station, Unit 4, November 2002 .... A-18

Figure A-8 Conductivity of Polished Water During a Condenser Leak at Callide C Power Station, Unit 4, November 2002 .... A-19

LIST OF TABLES

Table 2-1 Benefits and Concerns Relative Mixed Beds v Separate Bed Condensate Polishers 2-8

Table A-1 Sources of Resin and Polisher Effluent Contamination.. A-21

1

BACKGROUND TO THE USE OF SEPARATE BEDS IN CONDENSATE POLISHING

1.1 EPRI Interest in the Application of Separate Bed Condensate Polishing on Fossil Power Stations

The purification of condensate being returned to fossil power station boilers by the continuous use of beds of ion exchange resin in the process termed condensate polishing is recommended by EPRI and described in the literature that it offers to its members. This advice is widely accepted and condensate polishing is well established. It developed in the early 1950's with the use of deep beds of mixtures of bead form anion and cation ion exchange resins that were regenerated on-site. Since that time many variants of the basic process have been introduced including, but not limited to, cation-mixed beds, separate beds and installations employing disposable powdered resins. Nevertheless, over fifty years later, the use of simple mixed beds remains the approach most widely used by fossil power stations as it has a lower capital cost than most other deep bed designs and is of proven effectiveness.

In recent years new demands have been placed on operators of power stations including pressure to reduce:

- all generating costs
- staff numbers
- quantity of chemical waste being discharged.

This situation has caused EPRI to review condensate polishing processes in a search for one that will provide polished water of a sufficient quality for fossil fired units but is less demanding on operator time than the designs currently favored by power stations. The use of separate beds, i.e. a cation removal stage followed by anion removal, and in most cases by a trail cation exchange bed, predates mixed beds for demineralization although the latter quickly became the preferred process for the final stage in any water purification process including condensate polishing [1,2]. Separate bed polishing plants lack the ability to yield the ultra pure water demanded by nuclear power stations. However, they have been shown to be able to produce a perfectly acceptable quality of condensate for fossil power stations and are claimed to be simpler to operate. Their use may be even more advantageous if the condensate polishing plant is to be operated in the ammonium form [3].

1.2 The Use of Separate Beds of Resins in Separate Service Vessels of a Conventional Design

1.2.1 An Early Design Proposal

Although mixed beds were adopted at a very early stage in the development of condensate polishing interest has been shown over the years in reverting to the use of separate beds of resins. Shivers and his colleagues considered the merits of a two bed cation-anion system for condensate polishing in 1975 [4]. They predicted that a simple cation-anion design would offer many benefits relative to using a mixed bed. They also recognized that separate beds could be less demanding to use than mixed beds particularly when operating in the ammonium form.

1.2.2 Studies at KEMA

KEMA, the research and consulting organisation based in the Netherlands, showed interest in separate bed polishing in the 1970-80's. Its work resulted in the adoption of a cation-anion-cation polishing plant at Pen Power Station, Velsen, Netherlands. This unit employs oxygen treatment with ammonia levels of 100 ppb [5].

1.2.3 Power Station Experience in The Use of Separate Beds/Separate Vessels in Condensate Polishing

1.2.3.1 German Power Stations

Some power stations in Germany have also adopted separate bed condensate polishers with the main source of information being the papers written by Bursik and De Dardel relating to experience at the large Mannheim Power Station [6]. They showed that in 1968 a design of polishing plant consisting of a cartridge filter, sand filter, cation bed and a mixed bed was used. A plant installed in 1972 used a simplified design consisting of a cartridge filter and a mixed bed. Later, in 1982, separate beds were introduced but these were still preceded by a cartridge filter and finally in 1997 the design was further simplified to a 1.63 m (64.2 inches) deep cation bed, a 1.03 m (40.2 inches) deep anion bed and a trail cation bed of 0.77 m (30.3 inches). The lead cation bed invariably becomes contaminated by corrosion products and this debris is removed in the normal way by back-washing before the resin is regenerated using hydrochloric acid. The regeneration is performed, down-flow and in-situ. The anion resin and the trail cation resins are treated using in-situ counter current regeneration [7]. Figures 1-1, 1-2 and 1-3.

The conductivity of polished water achieved from the later polishing plant at Mannheim was < 0.06 μS/cm @ 25°C with sodium levels of < 0.5 μg/kg (ppb). These plants are operated in the H-OH mode and not beyond the ammonia break. The purity of the polished condensate is certainly acceptable for the majority of fossil stations but not any better than could be expected from a well run simple mixed bed polisher the capital cost of which would, based on EPRI estimates, probably be about two thirds of the separate bed cost [8]. Thus, its advantages relative to the commonly used mixed bed must be critically examined. If it is easier to use this could be a significant benefit particularly if it does not require specially trained plant operators. However, the capital cost will remain a disadvantage.

The design of separate bed polishers used in Germany would, if sulfuric acid was being used as the cation resin regenerant, lend itself to simpler operation in the economical ammonium form although, as discussed below, counter-current regeneration will not offer any particular advantage. In-situ regeneration, whether used conventionally as down-flow or as counter-flow is, however, viewed with distrust by utilities in most other countries as they have concerns about possible regenerant leakage into the steam/water circuit. It has been reported that one such incident occurred in about 1977 when sodium hydroxide entered the steam/water circuit of a 320 MW unit causing serious damage to the austenitic reheater and the turbine that took four months to repair. Following this incident recommendations were made by the VGB aimed at preventing similar occurrences. This involved the installation of a three valve assembly into the regenerant lines consisting of two isolation valves and one relief valve. The arrangement is sometimes referred to as "block and bleed". Further safety measures are also taken [6]. Figure 1-4.

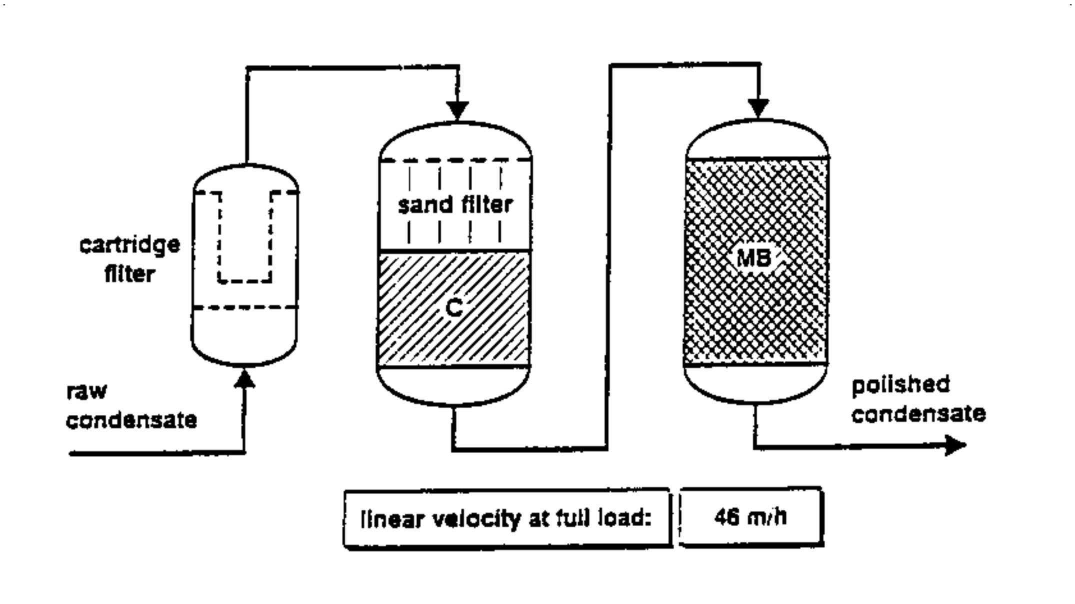

Figure 1-1
Design of Mannheim Deep Cation-Mixed Bed Polishing Plant, 1968

Source: Condensate Polishers in Separate Bed Configurations, Fifth EPRI International Conference on Cycle Chemistry in Fossil Plants, Charlotte, 1997

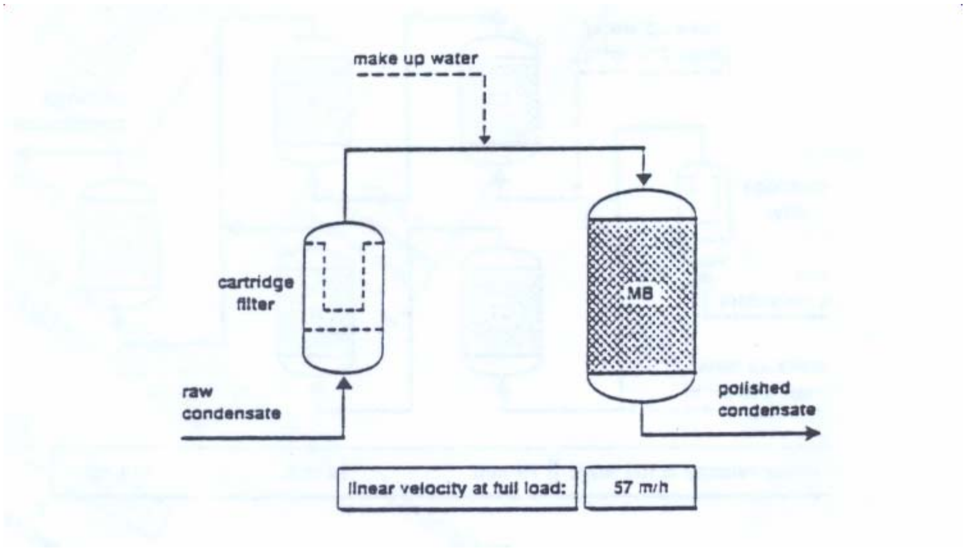

Figure 1-2
Design of Mannheim Deep Mixed Bed Condensate Polishing Plant, 1972

Source: Condensate Polishers in Separate Bed Configurations, Fifth EPRI International Conference on Cycle Chemistry in Fossil Plants, Charlotte 1997

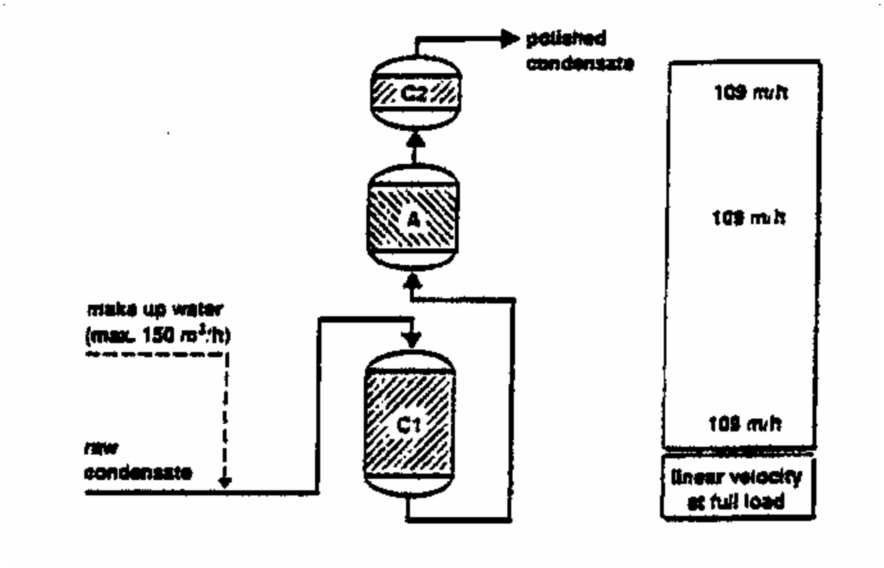

Figure 1-3
Design of Mannheim Deep Separate Bed Condensate Polishing Plant, 1997

Source: Condensate Polishers in Separate Bed Configurations, Fifth EPRI International Conference on Cycle Chemistry in Fossil Plants, Charlotte 1997

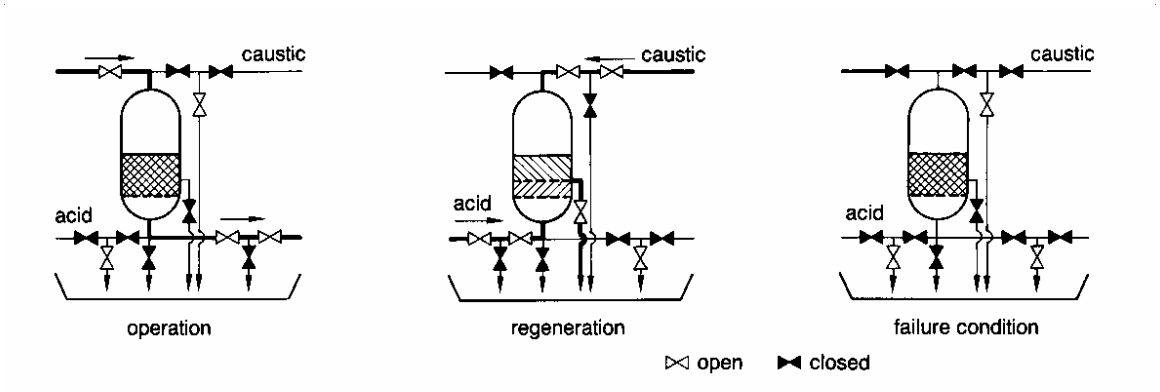

Figure 1-4
Three Valve Arrangement on Regenerant Lines to Separate Bed Polishers Using In-Situ Regeneration

Source: A. Bursik and F. de Dardel, "Comparative Evaluation of Condensate Polisher Design and Performance", Proc. International Water Conference, 1989

1.2.3.2 Danish Power Stations

Recent examples of separate bed/separate vessel condensate polishing plant designs are those known to be installed on two new 400 MW ultra supercritical sister stations, Energi E2 and Elsam, owned by Danish utilities. The polishing plant on the Elsam station uses in-situ regeneration with that on the Energi 2 station employing external regeneration so providing an interesting comparison of the two regeneration techniques [9]. The polishing plant consists of a lead cation exchange vessel, an anion vessel and a trail cation exchange vessel. This trail bed is only normally used immediately after resins from the preceding beds have been regenerated and until sodium levels fall below 1µg/kg (ppb). It is by-passed in normal operation as Elsam believes that sulfonate impurities released from cation resins in condensate polishers caused sulfate contamination and deposition in the steam/water circuit of at least one of their power stations.

It is of course possible to measure levels of sulfonate in condensate and studies have been made of the pickup of this impurity across the trail cation resin layer in a prototype Tripol^{R} separate bed condensate polishing system. These were made using a technique developed by Southern California Edison and showed very little sulfonate pickup during normal operations, i.e. 0.1 to 0.2 µg/kg (ppb). The technique involved first determining the sulfate level in the condensate sample by the use of ion chromatography followed by a second analysis after the sample had been radiated with ultra-violet light [19].

Despite the differences in the mode of regeneration between the polishers on these sister power stations the basic designs used are very similar. It is therefore not surprising that the published results show that the quality of the polished water is very similar with impurity levels of 0.29, < 0.1 and < 0.1 µg/kg (ppb) being shown for sodium, chloride and sulfate respectively on the counter-current regenerated plant and < 0.1, 0.29 and 0.19 µg/kg (ppb) for these impurities on the externally regenerated separate bed plant. Based on these figures, the in-situ counter-current regenerated plant is performing marginally better than the externally regenerated plant if the claim that its measured sodium level is biased high is accepted. In fact both are producing polished condensate of a quality that comfortably exceeds current target guidelines and are an order of magnitude below the 1st EPRI Action Level. However, it has been shown to be possible to routinely produce polished condensate of significantly higher quality when using a plant involving a mixed bed [10,11]. Although mixed beds have this capability it must be pointed out that qualities actually achieved by fossil power stations vary with some reporting a performance markedly inferior to that shown by the Danish separate bed plants. It is believed that this is because the performance of mixed beds is very dependent on the design and operation of the regeneration plant.

EPRI estimates indicate that the capital cost of a separate bed/separate vessel polishing plant is 50% more than that of a comparable simple mixed bed plant. When comparing benefits and disadvantages of different polisher designs, the issue of cost is important. Regenerations will be relatively infrequent assuming that low ammonia levels are being used by the Danish OT conditioned units. Manpower demands should therefore not be high but equally, the effort demanded by a mixed bed plant would also be low. The sulfate deposition problems that occurred around the steam/water circuits on an earlier unit in Denmark remains a cause for concern for the Elsam management and has clearly influenced their design approach. Apart from possible sulfonate leakage minimization, the main advantage of the separate bed polishing plants is probably the ease of regeneration and the avoidance of the need to provide and use specialized systems for separating mixed beds. For stations using higher ammonium levels in their condensate, operation in the economical ammonium form would result in significant savings and these would off-set the increased capital costs of a separate bed/separate vessels polishing system. It is reasonable to believe that counter-current regeneration results in some improvement in the quality of the final polished water but it can only be used on in-situ regenerated plant and this is unacceptable to the majority of operators of large power plants. Furthermore the advantages of counter-current regeneration are likely to be lost if the polishers are operated in the ammonium form as any impurities remaining in the upper levels of beds will be displaced during on-line ammoniation.

1.2.3.3 South African Power Stations

Eskom, the South African power utility, uses condensate polishing on all its large fossil fired boilers. In the 1980's it commenced building three very large air cooled power stations, each of approximately 4000 MW, sited in areas with ample coal reserves but where the water resources are very limited. These six unit stations have, of necessity, to use dry cooling so that the impurity loads placed on their condensate polishing plants differ from that on stations using water cooled condensers. Ammonia levels giving pH 9.8 together with OT are now used to minimize iron pick-up from the 80,000 m^2 surface area of carbon steel in each air condenser. Levels of iron in condensate entering the polishing plant are typically in the range of 2-12 μg/kg (ppb) and those in polished water are typically between 0.2 and 4 μg/kg (ppb) [12]. Air in-leakage into the vast condensers poses another problem as the carbon dioxide in this air increases condensate cation conductivities above the levels permitted by the manufacturers of the turbines. Thus, the polishers have to act both as efficient filters and also to remove carbon dioxide in a condensate that is much warmer than experienced on more conventional power stations [13]. Condensate temperatures range from 40 to 80 °C (104 to 176 °F) with the conventionally accepted limit for anion resins being 60 °C (140 °F). Eskom has overcome these problems by using separate cation and anion resin beds in separate vessels. Sodium leakage from traces of regenerant sodium hydroxide retained by the anion resin is minimized by special rinse techniques allowing the polishers to be operated in the ammonium form. When operating in the H-OH mode, sodium levels in polished condensate were about 0.4 μg/kg (ppb with chlorides 0.03 μg/kg (ppb) and a cation conductivity of 0.065 μS/cm.

The sulfate leakages are also low considering that the cation resins are regenerated with sulphuric acid. Studies were in fact carried out on the release of sulfate from the lead cation bed when operating in the H-OH form at high temperature. They showed that it varied from about 1 μg/kg (ppb) at 45 °C (113 °F), to over 5 μg/kg (ppb) at 75 °C (167 °C) indicating that the ionic load on the following anion resin bed varied with temperature. These polishers are now operated in the ammonium form and it would be interesting, in view of the results reported by Southern California Edison, to repeat these sulfate leakage studies.

The efficiency with which these separate bed polishers removed iron was studied during the commissioning of Matimba power station. The results showed that under steady state conditions with inlet iron vales of 19-41 μg/kg (ppb) removal efficiency was between 80-90%.

Under very arduous conditions the separate cation-anion condensate polishers are performing well on these South African dry cooled power stations indicating that even better performances should be expected by similar two stage plants running under less demanding conditions. More detailed information on impurity levels currently being found in the polished water from these two stage, separate bed/separate vessel, polishing plants would be of considerable interest.

1.3 The Tripol^R System

1.3.1 Development of the Process

1.3.1.1 Preliminary Studies Using Small Scale Separate Columns

An interesting variant to the separate bed approach to condensate polishing was proposed in 1980 by Smith and Peploe and termed Tripol^R. They proposed a design in which layers of cation, anion and cation resins were contained in a single vessel in shallow beds with a total bed depth similar to that used in mixed beds, i.e. 1–1.5 m. (39.4 –59.1 inches). Their experimental work included operating a laboratory rig using separate cation-anion-cation 50 mm (2 inches) diameter glass columns at linear velocities up to 200 m/h (83 gpm/ft^2). This velocity must be compared with that used on conventional condensate polishing plants of about 120 m/h (50 gpm/ft^2) and that on the 1995 separate bed polisher at Manheim of 109 m/h (45 gpm/ft^2) Tests were performed both in the laboratory and when drawing condensate from a 500 MW unit on an oil fired power station. The results indicated that condensate of a quality suitable for use on fossil power stations could be produced with levels of impurities such as sodium rarely exceeding 1 μg/kg (ppb) even when operating in the ammonium form at pH 9.4 [14].

1.3.1.2 Pilot Plant Tests

To further the development of the layered separate bed system four separate trials were carried out using 1 m (39.4 inches) diameter prototype vessels. Figure 1-5. The earliest one carried out on Gladstone power station (Australia) by the developers of the system was encouraging as it showed that sodium levels of about 0.1 µg/kg (ppb) could be achieved when operating in the H-OH mode with, as expected, higher leakages being seen when operating at high pH in the ammonium form. Specific measurements of chloride and sulfate leakage were not made but the cation conductivities observed do not indicate high levels in the final polished water.[15] A second series of tests are reported to have been carried out at Vales Point power station (Australia) but details are not available. However, independent trials were later carried out, again using 1 m (39.4 inches) diameter prototype vessels, in the United Kingdom by the former CEGB and in the USA by Southern California Edison on behalf of EPRI. The results of these later trials have been widely published. The CEGB work essentially agreed with the findings of the earlier trials by the developer and concluded that this proprietary layered separate bed design was a practical form of condensate polishing for power stations requiring condensate containing less than 2 µg/kg (ppb) of the common impurities. [16,17].

The results of the more extensive EPRI sponsored trials carried out by Southern California Edison broadly agreed with those of the CEGB relating to operation in the H-OH mode although there were minor differences in the experimental arrangements. However, they clearly and consistently showed that under ammonium form conditions some leakage of sulfate could occur and this leakage became of much more concern when the polishers were being challenged by condensate affected by a simulated sea water leak. The specific cause of this observed leakage of sulfate from the trail cation resin remains unclear but a number of possible sources are discussed in the Appendix [18, 19]. The efficiency of this prototype polisher was also examined by SCE for the removal of corrosion products with the results showing with an influent of about 40 µg/kg (ppb) iron the removal efficiency was approximately 55%. This work was performed on a power station and the removal efficiency observed was comparable to that being obtained by the stations own filtration-mixed bed polishing plant.

The pilot plants tests are described in more detail in the Appendix.

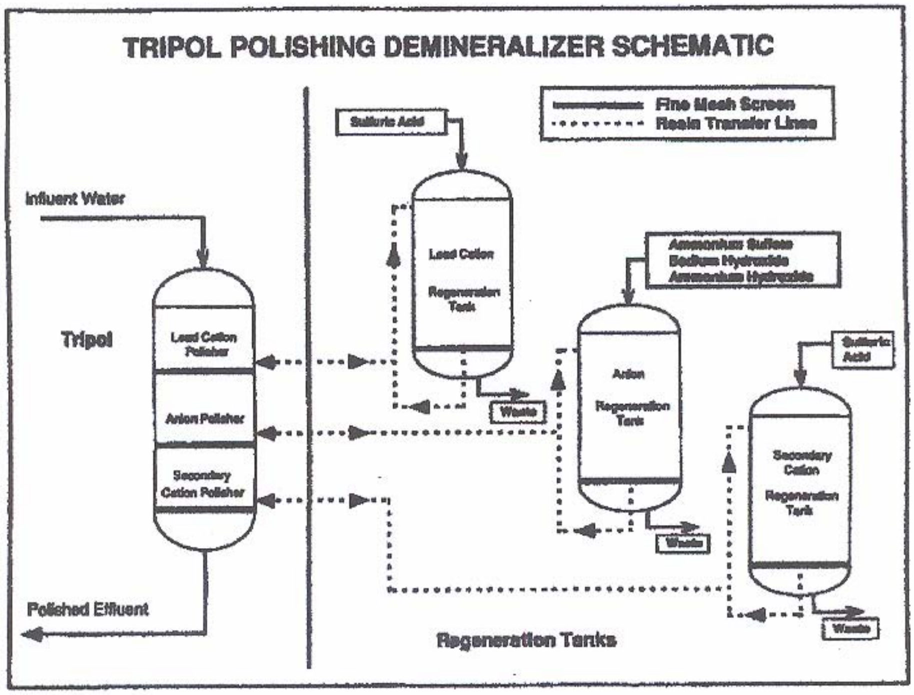

Figure 1-5
Diagram of Prototype Tripol^{R} Test Facility Used In SCE/EPRI Trials

Source: D.C. Auerswald, Proc. EPRI Condensate Polishing Workshop, Little Rock, Arkansas, 1989

1.3.2 Use of Tripol^{R} on Power Stations

1.3.2.1 Power Stations Using Tripol^{R}

There are now approximately 14 full scale layered separate bed plants operating on nine power stations and these have now accrued many years of operating experience. This design of condensate polishing plant has been installed and is operating at Collie, Callide C, Loy Yang, Muja, Stanwell and Tarong North power stations in Australia. It is also reported to be used on Suraya 2 power station in Singapore and, interestingly, has more recently been installed on a new CCGT power station at Huntly, New Zealand.

1.3.2.2 Callide C Power Station, Australia

Callide Power Plant was commissioned in 2001 and employs two once-through, coal fired, supercritical boiler units. These use cooling water that is itself cooled in towers taking make-up water from the Callide dam. The units were designed to produce 420 MW but now run at 460 MW. The steam/water circuit of each boiler is protected by one 100% flow (1152 m^3/hour, 5075 gpm) layered separate bed polishing plant. A separate regeneration facility services both of the units polishing plant resins. This consists of separate treatment vessels for the lead and trail cation resins with sulfuric acid being streamed from the trail cation vessel to the lead cation regeneration vessel. There is evidence of an imbalance between the two cation resin layers and it is thought that this may be caused by the use of a common transfer line. Rebalance operations are carried out at approximately six month intervals. Anion resin is treated in its dedicated regeneration vessel using sodium hydroxide regenerant in the conventional manner. Spare charges of lead cation resin, anion resin and trail cation resin are held (one charge of each) and are rotated through both units with a regenerated charge being held in the regeneration area in preparation for transfer.

Tests to monitor the condition of the resins being used have not yet been carried out but there are proposals to start such tests. Other issues include fouling of the lead cation resin layer at start-up with some crud slip into the anion resin and trail cation resin layer. Contamination of the trail cation resin by crud is undesirable as it may retain traces of sulfate from contact with the sulfuric acid used as the cation resin regenerant. Sulfate contaminated crud may, as discussed in the Appendix, lead to enhanced leakage of the impurity into the final polished water. Problems with ball valves have been encountered at Callide C. These are considered to be caused by actuator air pressures being inadequate [20].

The unit is operated at pH 8.9 so that the polishers, when operating in the H-OH mode, have service runs of about 3-4 weeks. The polished water is reported to have sodium levels of less than 1-2 µg/kg (ppb). In November 2002 one of the units experienced a large condenser leak that resulted in the influent conductivity being > 10 µS/cm resulting in both the direct conductivity and the cation conductivity increasing to about 0.2-0.3 µS/cm peaking at 0.6-0.7 µS/cm. This condenser leak was a severe test of the station's separate layered bed condensate polishing system. Conductivity measurements indicate that under these challenging conditions it removed approximately 99% of the influent ionic impurities. Unfortunately, information on the actual concentrations of the individual impurities in the polished water is not available and so these have to be estimated from conductivity readings. The performance of the Callide layered separate bed polisher is obviously of importance as it could give an indication of what can be expected when polishers of this type are treating condensate with very high influent impurity levels.

It is interesting to speculate whether an even better performance could have been achieved at Callide or whether a conventional mixed bed would have shown a superior performance. Many tests have been carried out in which mixed bed polishers have been challenged with condensate containing up to about 1 mg/kg (ppm) of ionic impurities but few tests are recorded to have been carried out under higher inleakage condition. Information is even harder to find on the performance of separate bed plants although during the early tests of a prototype Tripol^{R} vessel an influent containing 500 µg/kg (ppb) of sulfate was used. In this case the polisher effectively removed the impurity with 1 µg/kg (ppb) of sulfate being found in the effluent. Challenge tests using condensate containing 380 µg/kg (ppb) have, as described below, been more recently carried out at Stanwell and, again, effective removal was seen with levels in the final polished water being < 1 µg/kg (ppb). The behaviour of the polishers at Callide during the condenser leak are further discussed in the Appendix.

It is also of interest that a very high in-leakage of cooling water, again derived from a cooling tower system with river water make-up, occurred on a PWR in the USA under circumstances similar to those seen at Callide.[21] In this case, the inlet sulfate levels were estimated to be 8.15 mg/kg (ppm) with levels in the water from their mixed bed polishers being 20-25 µg/kg (ppb). This incident caused sulfate levels in the steam generator water to increase to a maximum of 600 µg/kg (ppb) although sodium and chloride levels showed little increase.

1.3.2.3 Loy Yang B Power Station, Australia

Loy Yang B power station employs 2 x 500 MW brown coal fired, sub-critical, once-through boilers commissioned in 1993 and 1996. Oxygen treatment is used at pH 8.5. Three 60% Tripol^{R} layered separate bed vessels are provided for both units These polishers are positioned on a 120% flow by-pass loop with two vessels being used in service and one acting as standby. What is described as a deep bed "prefilter" is used in front of the actual polishers for start-ups and shutdowns. This prefilter is essentially a cation exchange bed that is capable of treating approximately 60% of the MCR condensate flow. Service runs of approximately 1000 hours (42 days) are obtained with polishers then being withdrawn for regeneration before ammonia breakthrough This run time was selected on the basis of the pressure drop across the beds and "*issues such as sticking valves due to the extended time between regens*". Each boiler unit has its own regeneration facilities that consist of an anion regeneration vessel and a cation vessel in which both the lead and trail cation resins are treated. In this the lead cation resin is first cleaned and the trail cation resin then subsequently added. The trail cation resin is then cleaned prior to both charges being regenerated together. The trail and then the lead charges are then transferred separately back to a holding vessel. Polished condensate from these polishers has a sodium level of < 1 µg/kg (ppb) and a cation conductivity of 0.05- 0.06 µS/cm indicative of very low chloride, sulfate and carbonate leakage, i.e. <1 µg/kg (ppb) [22]. On-line sulfate challenge tests have been carried out in order to check that the anion resins have not become kinetically impaired.

1.3.2.4 Stanwell Power Station, Australia

Stanwell Power Station commissioned four coal fired drum boiler units, each designed to produce 350 MW of power, between 1992 and 1996. These units are intended to be upgraded to 378 MW following turbine blade modifications. The boiler units were all provided with full condensate polishing in the form of a single 100% flow Tripol^{R} layered separate bed system. One regeneration plant was provided to serve all four polishers and consists of a single cation regeneration vessel, in which the lead and trail cation resins are treated, and an anion regeneration vessel. A spare resin charge is held. The station uses cooling water drawn from cooling towers with make-up from the Fitzroy River. The river contains very high levels of a fine clay suspended matter. Traces of this material can enter the steam/water circuit through condenser leaks and, as it is not removed by the polishers, it becomes thermally degraded so causing high silica levels in boiler water. Stanwell was commissioned with aluminium brass LP feedheaters with cupronickel tubes installed in the air extraction zones of the condenser and commenced operations using conventional AVT boiler water treatment. Flow assisted corrosion was noted immediately so between 1996 and 1998 the feedheaters were re-tubed with 304 stainless steel and Oxygen Treatment at pH 9.38 was adopted and is still used.

The lead cation bed depth is 349 mm (13.7 inches) while the trail cation bed has a depth of 334 mm (13.1inches). The anion bed is 449 mm (17.7 inches). The resin layers rest on laser cut stainless steel screens. Each vessel has a diameter of 2800 mm (110.2 inches). Figure 1-6. The original inlet distributor design consisted of five radial arms but this resulted in disturbance being caused to the lead cation resin layer and to low capacities being achieved. The inlet distributor was successfully modified with the result that the capacity of the polisher to the ammonia break and to full ammoniation was significantly increased from the earliest value observed. A further commissioning problem was encountered in that the transfer of resin from the service vessel to the regeneration facility was incomplete. An inner water ring main that was supplied from the outer ring main was added. This, together with modifications to the flow of the bottom transfer water, allowed “complete” resin removal. The lead and trail cation resins are regenerated in the same vessel with the trail cation resin placed on top of the lead cation resin. In this position the down flow of the regenerant sulphuric acid is streamed though the trail resin and passes to the lead resin. The lead cation resins can be cleaned and regenerated by themselves if required [23].

Gel resins have always been used in the polishers at Stanwell and these have had life times of between 6 and 10 years. It is to be noted that condensate temperatures can, in summer time, be in excess of 50 °C (122 °F). Resins tests are carried out regularly by a contract laboratory and, as detailed below, plant challenge tests have also been used. Resin cross contamination has not been observed.

The polishers were intended for operation in the ammonium form and were specified with this purpose in mind. The early report describing their use stated that when operating in the ammonium form, at pH 9.34 - 9.38, sodium levels of 0.2-0.4 µg/kg (ppb) were obtained with 0.2 ppb µg/kg (ppb) of both chloride and sulfate. The polishers usually run for about one week prior to ammonia breakthrough occurring and are then kept in service in the ammonium form at pH 9.38 for a total service run of ten weeks.

A problem of high silica levels in the boiler water was initially observed but this has corrected itself and is assumed to have been a post commissioning issue. In recent times, elevated drum silica levels have been increasingly observed towards the end of a polisher 10 week service cycle [24]. These high levels are effectively reduced when the condensate polishing resins are replaced by regenerated resins. It is currently assumed that the silica involved originates in trace leakage of this impurity through the demineralisation plant.

Condensate dosed with 380 µg/kg (ppb) of sulfate has been used as part of an on-line check on anion resin exchange kinetics. During these challenge tests sulfate levels in polished water have not exceeded 1 µg/kg (ppb) which acts to confirm that resin kinetics were at the time still acceptable. It is also reported that “the station has experienced a number of condenser leaks where significant ionic loadings were placed on the vessels at no stage has any sort of breakthrough been observed”. High cation conductivity levels in polished water have, however, been seen in the 6 to 12 hours following the return to service of freshly regenerated beds. The cation conductivity of the polished condensate was seen to increase by approximately 0.03 µS/cm and this was associated with a dramatic rise in boiler water cation conductivities that required heavy blowdown to control the situation. Analysis showed boiler water sulfate levels to be up to70 µg/kg (ppb) but detailed analyses of the condensate and feedwater during this period were not carried out. Thus, the source of the sulfate was not clearly established and may have been caused by incomplete rinsing or from sulfonate released by the trail cation resin bed. This sulfate release problem was not a continuing one so that the possibility of sulfonates being the cause is less likely as their release should have been an almost steady effect. Nevertheless they cannot be excluded although station investigations centred around regeneration rinsing procedures. After a change of resins a different problem, that of high chlorides in boiler water, was experienced that demanded an increase in blowdown requirements. The use of this high blowdown rate also reduced sulfate levels so they became, for a time, less apparent. However, chloride release from the new resins decreased over a 12 to 18 month period and sulfate once again became the main impurity in boilerwater although it is not high enough to be of operational concern [25].

Sulfonate/sulfate leakage has not been reported from the other Australian power stations using separate layered bed polishing plants that have cooperated in this review, i.e. Callide C, Loy Yang and Tarong North. These stations are, however, all equipped with once-through boilers so sulfate concentration in boiler water is not a concern. Even if sulfonate leakage is taking place from polishers on these stations it is unlikely to be detected unless sulfate balances are measured across a boiler or special investigations are carried out using sensitive analytical procedures. Experience shows that sulfonate leakage varies from resin type to resin type and also with the condition of the resin. As already mentioned, during the earlier studies carried out on behalf of EPRI by Southern California Edison a 1 m (39 inches) diameter prototype Tripol^R was used. Using the technique for measuring sulfonate levels in condensate that has already been described it was shown that levels of sulfonate in the polished condensate from the prototype vessel were about 0.1 to 0.2 µg/kg (ppb) [19]. The levels from mixed beds should be lower, assuming beds are well mixed, because some of the sulfonate will be held by the anion resin present in the bed. The release of sulfonates is a complex issue that even now is not fully understood although resin manufacturers are fully aware of the demand for "clean" resins. Fortunately, plant problems have only been seen in a few cases but stations must be aware of this potential problem. Sulfate and sulfonate release is further discussed in the Appendix.

Although the mechanical features of the Tripol^R units at Stanwell are considered to be robust a small puncture of one of the resin support screens was however found and presumed to have been caused by mechanical damage such as a dropped tool. It was also reported that the support/seal arrangement around the outside edge of the screen was subject to some disturbance with the passage of time [25]. Lack of access facilities to the individual layers has been pointed out as a disadvantage, one that Stanwell has remedied. Other users of Tripol^R have expressed a preference for separate lead and trail cation regeneration vessels in place of the existing common vessel. The later plants at Callide, Tarong North and Huntly, New Zealand, in fact now use separate lead and trail cation regenerators. Iron fouling of windows has also been pointed out as another problem as it interferes with visual inspections of the resin layers. A similar effect has been reported by users of other designs of condensate polishers and is possibly exacerbated by the use of Oxygen Treatment. A procedure or technique to overcome the problem would obviously be useful.

Overall, the polishing plants at Stanwell, which are largely automated, are considered by their staff to be "very beneficial" and "easy to use" [25].

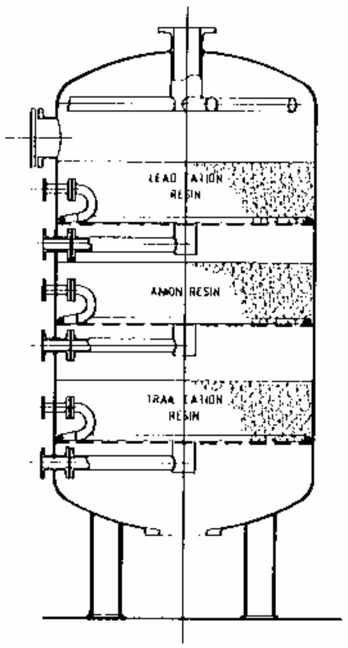

Figure 1-6
Tripol^{R} Vessel Used at Stanwell Power Station, Queensland Australia

Source: S. Kerr, "Tripol Condensate Polishing at Stanwell Power Station: Six Years of Operational Experience", Power Plant Chemistry, 2000, 2(7)

1.3.2.5 Tarong North, Australia

Tarong North Power station was commissioned in 2003 and uses cooling water drawn from fan assisted cooling towers that take makeup from the Wivenhoe dam. The station has one 450 MW once-through supercritical unit the steam/water circuit of which is protected by a single, 100% flow, layered separate-bed condensate polishing vessel operated in the H-OH mode. The condensate pH is 9.0 and the flow through the polisher is 1080 m^3/hour (4758 gpm). The polisher resins are regenerated in a plant consisting of separate vessels for the lead and trail cation resins and a vessel for anion resin regeneration. Resins are tested annually by a contract laboratory for physical properties and for capacity.

The levels of sodium, chloride and sulfate in the final polished water are reported to be < 0.5 µg/kg (ppb) with cation conductivities of 0.06-0.07 µS/cm. It is considered by staff at Tarong North that the Tripol system is successful and has been well accepted by the operators. It has not presented on-going difficulties although some problems have been encountered with ancillary equipment such as regeneration injection pumps [26].

1.3.2.6 Huntly e3p Project, New Zealand

As an expansion of an existing power station at Huntley, Genesis Energy has installed a 400 MW Combined Cycle Gas Turbine (CCGT) employing cooling water drawn from cooling towers that use river water as make-up [27]. The utility had evidence that it had obtained significant benefits from the use of condensate polishing on the existing four Huntly power station units. Nevertheless, a searching within company review of costs and benefits associated with the provision of condensate polishing to protect the new CCGT unit was carried out. This finally led to the decision to install a Tripol^R layered separate bed polishing plant.

The condensate flow on Huntly e3p heat recovery steam generator was lower than on the Australian power stations discussed above but the design of the polishing plant broadly followed the design used on the later plants and consisted of:

- a single skid mounted service vessel that was sized to accept 100% condensate flow,
- a skid mounted regeneration assembly with separate vessels for the lead and trail cation resins and for the anion resin
- storage facilities for the regenerated spare resin charge

However, the depth of the resin beds is greater than on other Tripols with all three beds being 500 mm (19.7 inches) deep and separated by laser cut screens. The linear flow through the vessel is 137 m/h (55.9 gpmft^2) in contrast to the 176 m/h (71.8 gpmft^2) used at Stanwell. As deeper resin layers are used at Huntly the anion resin specific flow ratio (condensate m^3/resin m^3) is 272 compared to 393 at Stanwell. It is possible that the difference could help to mitigate the effects of any loss of anion resin kinetics that usually arises as resins age or become fouled.

The plant is guaranteed to yield polished condensate with levels of sodium, chloride and sulfate of less than 1 μg/kg (ppb). It is also guaranteed to have a filtration efficiency of 90% for the removal of crud particles of less than 10 microns. The utility intends operating the steam/water circuit using an All Volatile Treatment at pH 9.6-9.8 without the use of reducing agents, i.e. using AVT(O). Preliminary information on the actual performance of this new plant reports that when operating in the ammonium form at pH 9.8 the sodium levels in polished condensate are < 0.1 μg/kg (ppb) with cation conductivities of 0.06 μS/cm. The latter measurements indicate levels of the common anionic impurities to be < 1 μg/kg (ppb), an indication generally confirmed by later ion chromatographic analysis [28].

The condensate polisher is regarded by Huntly staff to be useful and simple to use with plant operators viewing it favourably. Comments on the overall plant include the need for more instrumentation such as silica meters on the polisher outlet in addition to the existing conductivity and sodium meters.

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2
DISCUSSION OF POLISHING AND THE ROLE OF SEPARATE BEDS IN FOSSIL PLANTS

2.1 Deep Separate Condensate Polishing Plants

Two general designs of separate bed polishing plants are in use, namely deep beds and a proprietary layered bed system. As already discussed, deep bed plants involve the use of cation-anion-cation resins in series with each resin contained in a separate vessel which is normally of a conventional design. Different methods are in use for the regeneration of the resins with at least one plant favoring external regeneration with resins being moved to the regeneration plant and then back to the service vessel. In-situ regeneration of resins is used in Germany and some neighbouring countries with some plants also using counter-current methods on the anion resin and trail cation resin. The quality of the condensate on a station employing polishers of this type has been reported as < 0.06 µS/cm, cation conductivity and < 1 µg/kg (ppb) sodium [1].

A variant of the deep separate bed approach to condensate polishing was adopted by Elsam, a Danish utility, for an ultra supercritical power station. Although a deep bed polisher of conventional design was provided, the station only normally uses the lead cation bed and the anion bed. The trail cation resin bed is brought into service if sodium levels in condensate after the anion exchange stage exceed 1 µg/kg (ppb). This is, of course, essentially a cation-anion separate bed system and when running in the H-OH mode levels of < 0.1 µg/kg (ppb) of chloride and sulfate and very low levels of sodium are achieved [2]. As already mentioned, two stage (cation and anion) deep bed polishers have been successfully used for a number of years by Eskom, South Africa, on its large, air cooled, coal fired power stations. When running in the H-OH mode and at temperatures of up to 80 °C (176 °F), they yield polished water containing sodium levels of about 0.4 µg/kg (ppb) and cation conductivities of 0.065 µS/cm [3].

Thus, polishing plants consisting of separate deep beds of cation and anion resins in separate vessels are currently being used and have been in service for many years both in the H-OH mode and in the ammonium form so that the adoption of this simplified approach would not represent an innovative step for power stations. The advantages in using separate beds of ion exchange resins in conventional service vessels include the ability to employ greater volumes of resins than employed in simple mixed bed polishing plants and also in polishers of the proprietary layered separate bed approach. Such deep bed plants can also make use of established vessel designs. The linear flows through these deep beds will, because of the increased pressure drops, be significantly lower than those normally used on layered separate bed polishers. Thus, a flow of approximately 91m/h (37.1 gpm/ft^2) is used on the cation-anion separate bed plants at Matimba, Eskom, (South Africa) with 109 m/h (44.5 gpm/ft^2) being used on the cation-anion-cation polishers at Mannheim [3,4]. These linear velocities are in contrast to the 176 m/h (71.8 gpm/ft^2)

used on the Stanwell layered separate bed polishers [5]. If polishers employing separate beds in separate vessels are to be used, rather than the proprietary layered separate bed design, then there will obviously be a need to provide larger diameter vessels or additional vessels for any given situation. Thus, a layered separate bed plant is likely to have a smaller footprint.

2.2 Design and Operation of Tripol^R Polishing Plants

The main purpose of the series of pilot plant trials described in the Appendix was to give confidence to proceed with the development and adoption of a full scale layered separate bed condensate polishing system. With a few reservations this objective was achieved and there are now believed to be fourteen layered separate bed polishers in operation on power stations with the earliest one at Muja, Western Australia, dating back to the early 1980's. The way in which the system has been applied has varied slightly with Loy Yang using three polisher vessels/unit for each of its two 500 MW boiler units with two in service and the third on standby. This conservative layout is similar to that used on most stations with simple mixed beds and has the advantage of allowing one bed to be regenerated without losing the capability to treat 100% of the condensate flow. Prefilters are also used and both polishing plants have a dedicated regeneration facility. At Stanwell a more economical design was adopted with only one 100% flow vessel being used for each 350 MW boiler unit and with one regeneration plant being provided to serve all four polishers. This plant was reported to have "the lowest capitalised costing" presumably when viewed against those of competing mixed bed designs [5]. Genesis Energy, New Zealand has recently selected a very similar layout of Tripol^R polishing plant for its new 385 MW CCGT unit that was built on an existing power station site at Huntly. It has been stated that "there was little capital cost difference between a traditional mixed bed and a Tripol^R condensate polishing plant" [6]. It is therefore apparent that, for a given plant, the capital costs of proprietary layered separate bed polisher will be approximately the same as those of one using conventional mixed beds. It is also reasonable to expect separate bed/separate vessel polishers to be more expensive with 1996 estimates by EPRI suggesting a 50% increase.

The proprietary Tripol^R system is at the moment the only design of condensate polisher using relatively shallow layers of cation-anion and cation resins. As already discussed, it has been used in Australia for over twenty years but even now information on its behaviour is limited compared to that available, from worldwide sources, on the performance and problems of mixed beds. Nevertheless, the Australian experience that is available clearly indicates that this layered separate bed system is a viable approach to using condensate polishing on fossil power stations. Its adoption in preference to using a conventional simple mixed bed system may not result in any significant saving in capital costs but its apparent simplicity in operation, particularly when running in the ammonium form, is an operational advantage. Consideration must now be given to whether this proprietary system is the optimum design for separate bed polishers or whether further improvements could be made with the objective of still providing an easy to use and relatively low cost technique. Modifications to the regeneration system and access to the individual resin layers have already been mentioned. Thought must also be given to further simplifying the overall design to a cation layer followed by an anion resin layer. This would allow the number of support screens to be reduced from three to two and possibly the use of deeper layers of resins.

2.3 Separate Beds and Ammonium Form Operation

The advantages and disadvantages of operating polishers in the ammonium form have been discussed many times before [7]. The power industry is currently faced with the need to reduce all generating costs. This requirement leads to staff numbers on power stations being reduced and to efforts being made to maintain full availability by minimizing all forms of corrosion. The industry is also attempting to minimize the quantities of waste products that require disposal. Ammonium form operation (AFO) of condensate polishers is useful in helping any power station to meet the current demands but although many stations have successfully used the technique some others have experienced severe problems. It is thought that problems have arisen from a combination of causes including insufficient training of the staff concerned and the difficulties, on some plants, of regenerating mixed bed resins to the high standards necessary for AFO. The technique is of course unsuitable for stations suffering from frequent condenser leaks in view of the need to always use uncontaminated resins.

Another possible advantage of operating condensate polishers in the ammonium form rather than the H-OH mode has been mentioned by staff at Huntly CCGT power station. They noted that when running at very high pH, 9.6-9.8, in the H-OH mode, levels of ionic impurities in the steam/water circuit were higher than seen when using AFO. This improvement was attributed to the need for very much lower ammonia replacement requirements and could reflect on the impurity levels in the bulk ammonia or in the dilution water used [8]. Stations operating with lower pH levels in their steam/water circuits may not notice this effect as it will obviously depend on the quantities and purity of ammonia being added. It is, of course, always prudent to have a purity specification for chemicals being added to the steam/water cycle and to verify that the specifications are being met.

It is claimed that polishers of the layered separate bed design are less demanding to use than a mixed bed and this claim is supported by reports from the stations that have assisted with this review. This ease of use probably also applies to other variants of the separate bed approach to polishing and is clearly an important advantage. When they are being used in the ammonium form, the problems of resin cross contamination that can occur on mixed beds and the efforts needed to achieve a good mixed bed separation are avoided. However, it must be pointed out that there are detailed reports from many stations with mixed beds describing their successful use of AFO over many years and that several, well proven, high efficiency separation/regeneration facilities processes are now available.

The actual situation with respect to the use of ammonium form polishers is more complex than that briefly sketched above. Condensate polishers have an important and rewarding role to play at the start-up of any unit as they can significantly shorten the time taken and at the same time protect the steam/water circuit from the ionic and particulate impurities that may have entered the system during the shutdown period. In performing this duty the polisher resins will themselves pickup impurities. This is not of concern if they are being operated in the conventional H-OH mode as they should be firmly held throughout the remainder of the service run. However, if they are being used in the ammonium form there is a risk that some of this impurity burden will subsequently be slowly released affecting the quality of the polished condensate. The higher linear velocities used on the layered separate bed plants are likely to increase the speed at which any impurity displacement begins to affect the quality of the final polished water. Thus, the warning given by EPRI regarding cycling ammonium form condensate polishers is soundly based. Any station proposing to attempt to do so must be aware of possible problems [7]. It is of interest, therefore, that on some stations layered separate bed polishers are being successfully used in the ammonium form for "hot starts", i.e. after short shutdowns. The ability to do this avoids the need to replace resin beds with freshly regenerated resins and is clearly a benefit for the station but critically depends upon whether the resins remain free of ionic contamination at start-up. Of course, separate bed polishers allow conditioning or change-out of the lead cation resin during startup without having to treat the anion resin or the trail cation resin.

2.4 Regeneration of Separate Bed Resins

If a two layer (or two bed) polishing process is to be adopted thought must be given to minimising leakage of traces of retained regenerant chemicals from both the cation and anion resins but particularly from the latter. The fact that resins, or possibly foulants or degraded sites on the resins, have the ability to retain traces of the chemicals used for regeneration purposes is well known. The "retained" regenerants are subsequently released when the resins are in service so contaminating the water being treated. When resins are used in mixed beds this leakage effect is mitigated to some extent but on separate bed polishing plants special care will have to be taken. Procedures are known, such as ammonia washing of anion resins and soaking resins for long periods of time, but more effective and simpler techniques would be useful.

Sulfuric acid is the cation resin regenerant of choice in many countries but others prefer, or are obliged by supply and/or economic considerations, to use hydrochloric acid. This acid is an extremely effective regenerant and has the added advantage that it helps to reduce iron fouling of cation resins. However, if traces of it are allowed to remain on cation resins after regeneration and the resins are subsequently used in a mixed bed polisher being employed in the ammonium form, unacceptably high leakages of chloride will occur. Because of this, EPRI generally advises stations that use hydrochloric acid not to attempt to operate their mixed bed polishers in the ammonium form. This advice, although theoretically sound, prevents stations from operating in this economical and labor saving way. The mechanisms governing chloride leakage arising from retained traces of regenerant acid are well understood and suggest that it is likely that separate bed polishing plants could show similar effects if their cation resins are regenerated using hydrochloric acid. Chloride leakage problems from separate beds operating in the ammonium form and using cation resins regenerated with hydrochloric acid have not yet been reported possibly because the few countries that use this acid and separate bed polishers do not operate in the ammonium form (e.g. Germany, Denmark).

The development of simple ways of minimizing the retention of trace quantities of any regenerant used on ion exchange resins could be very useful and have wide application. Possible techniques include:

- Extended rinsing with long standing time
- Closed circuit rinsing of anion resins with a small cation resin bed in circuit
- Closed circuit rinsing of cation resins with a small anion resin bed in circuit
- Ammonia rinsing of anion resin on a closed circuit with an ammonium form cation bed (attention to sodium level of the clean-up cation resin necessary)

- Innovative approaches e.g.:
  - Ammoniating cation resins after regeneration with hydrochloric acid
  - Using a form of the “Resin on Resin” cleansing technique in which the purifying cation or anion resins are held captive in some manner, i.e. a porous removable containment [9]
  - Rinsing with water under an applied electrical field,
  - Displacing any sodium held on anion resins by a low level treatment with a selected amine such as diethylamine. Alternatively, weaker amines such as morpholine or ethanolamine may be beneficial. Health and safety issues will have to be considered if rinsing with amines is proposed.

2.5 Applicability of Separate Bed Condensate Polishers

In a recent report dealing with the “Condensate Polishing State of Knowledge” attention was drawn to the continuing need for its use on all types of fossil power stations and to the changing demands being made by utilities. It also pointed out that polishing plant designs have not markedly changed over fifty or more years in strong contrast to what has happened in other technologies [10]. Some possible lines of development were indicated and these may well come to fruition in future years but the fossil power industry currently needs an effective form of condensate polishing that meets its requirements until newer techniques become available. There is little doubt that mixed bed polishing plants can, assuming that they are well designed and operated, produce condensate of a higher quality than that so far achieved by designs of polishers using separate beds or layers of resins. Fortunately fossil stations are slightly more tolerant of impurities than most nuclear plants so that condensate suitable for their use can be obtained from separate beds. Their requirements have changed over the years and management is now driven more by operational factors than by consideration of condensate purity beyond their needs. Their current needs are for polishers that:

- are simple and robust to use and require little attention
- can be maintained by staff without specialised knowledge
- are capable of being automated
- produce minimal quantities of chemical waste as far as operationally possible

Both mixed bed and separate bed polishing plants can, with some exceptions, be used in the ammonium form. As already discussed, this results in very long service runs and hence fewer regenerations leading to significant reduction in the use of manpower, chemicals and the volume of chemical waste requiring disposal. Mixed bed plants can operate in the ammonium mode if special attention is paid to the critical stages of resin separation prior to regeneration and the regeneration procedures themselves. Separate bed plants, as shown in Australia, New Zealand and South Africa can relatively simply be regenerated to the level required for operation in the ammonium mode.

The question of when to recommend the adoption of separate bed plants rather than polishing plants of the more conventional mixed bed type has to be addressed. There is no simple answer but it is suggested that if a new fossil station intends operating its polishers in the ammonium form then a separate bed design should be considered. For new fossil stations likely to use their polishers in the as regenerated H-OH mode, such as those stations operating with low levels of ammonia in their steam/water circuits, mixed bed designs with effective resin separation/regeneration facilities may offer advantages. When it comes to retrofits the operating pattern of the station will have to be considered and particularly whether it regularly cycles or suffers condenser leaks. Polishing plants on those experiencing frequent startups often have to remove considerable quantities of particulate form corrosion products. Polisher beds then become contaminated with this debris leading them being frequently replaced by freshly regenerated beds or at least cleaned. Separate bed, cation-mixed bed or filter-mixed bed plants offer the advantage over those using unprotected mixed beds in that the cation resin in the leading bed or filter can be simply cleaned or replaced.

The use of off-site regeneration of resins by contractors has been suggested as a way of minimizing the effort required by stations to use and maintain condensate polishers. [11] The interest shown to date by power stations with existing polishing facilities has generally been low although it is noticeable that one major utility has adopted the approach. This is possibly because stations already have on-site the necessary regeneration equipment and this affects the economic case for changing to off-site servicing of resins. The viability of this approach for new stations or those retrofitting polishing obviously depends on the geographical location of interested stations and whether appropriate regeneration services are available. It may also depend on whether mixed bed or separate bed polishers are being considered. This is because one of the concerns raised about off-site regeneration has been whether the specialist contractors could, off-site, routinely and reliably separate and regenerate mixed beds to the degree that would allow them to be used at high pH in the ammonium form. If off-site regeneration is to be used it seems that separate bed polishers would be the better choice unless the contractor has specialized separation equipment.

The suggestion that separate bed polishers should be selected by stations wanting to operate in the ammonium mode, and mixed bed designs by those stations that will run their polishers in the H-OH form for several weeks as they are using low ammonia levels, is obviously simplistic There are examples of stations comfortably doing the reverse! Nevertheless, the suggestion is offered as a guide with the final decision by any utility hopefully being made in the light of EPRI advice and other information available.

The benefits and concerns relative to mixed bed versus separate bed polisher designs are summarized in Table 2-1.

2.6 Suggested Further Work

2.6.1 Collate and Share Operating Experience

The primary aim of any condensate polishing system is to consistently purify condensate to a degree that assists high pressure steam generators/boilers to function without corrosion or any other impediment to their availability or capacity. There seems little doubt that separate beds of ion exchange resins, in the absence of very high levels of impurities in the influent condensate will yield water with impurity levels well within any limits advised by EPRI. There is some evidence that they will also protect high pressure steam generators/boilers from the effects of massive ingress of impurities caused by incidents such as condenser tube leaks or breakage. However, despite separate bed condensate polishing having been in use on a variety of boiler types on three continents for over twenty years it has not been studied to the same extent as polishing processes using mixed beds of resins. Users should be encouraged to share their experience and to make known any difficulties that the encounter.

2.6.2 Ability of Separate Bed Polishers to Treat Very Large Condenser Leaks

The ability of separate bed polishers to treat reasonable levels of impurities in condensate has been satisfactorily demonstrated in trials but their behaviour in the face of massive leaks that can occur when several condenser tubes are ruptured has not been explored. It is unlikely that such tests will take place on polishing plants that are in operation but useful data could simply be obtained using existing computer models. If this is done it would be interesting to consider polishers operating in both the conventional H-OH mode and in the ammonium form. Comparisons with the behaviour of a typical mixed bed would also be of value.

2.6.3 Post Regeneration Resin Purification

The purity of the condensate yielded by any separate bed plant will depend on the efficiency with which the resins can be regenerated and cleansed of traces of regenerant chemicals. In particular the resins in the trail bed, whether this is cation resin in a three bed system or anion resin in a two bed arrangement, must be purified as far as possible. Although post regeneration resin purification processes are already being successfully used it is desirable that further attention be given to ways of minimising the retention and possible leakage of regenerant chemicals. Some possible approaches have already been mentioned and if they could be successfully developed they could have applications beyond separate bed condensate polishing.

Table 2-1
Benefits and Concerns Relative Mixed Beds v Separate Bed Condensate Polishers

Attributes	Mixed Bed		Separate Bed	
	Benefits	**Concerns**	**Benefits**	**Concerns**
Filtration, corrosion product removal	Different particle sizes of mixed cation and anion resins improve filtration.	Small layer of anion resin that typically forms at the top of the mixed bed often becomes permanently fouled with corrosion products.	Lead cation resin layer (or bed) does most of the filtration and removal of corrosion products, thereby protecting anion resins. Iron removal from cation resin is more easily accomplished.	Lead cation resin needs separate cleaning and regeneration (if possible) to avoid contaminating trail cation resin with corrosion products that may be a significant source of sulfate leakage.
Separation of resins for regeneration	Uniform particle sized resins and advanced separation system assist in providing adequate resin separation.	Great care must be taken to assure good separation. Even small amounts of residual cation resin in the anion resin layer may prevent operation in economical ammonium form unless post regeneration cleanup is utilized.	Resins do not require separation since they are never mixed.	Resin fines must be kept to a minimum to prevent migration of fines across stainless steel screens of layered bed design.
Normal in-service operation	Theoretically, mixed bed provides highest purity water.	Quality of effluent determined by efficiency of mixed bed separation prior to regeneration and thoroughness of remixing for in-service operation. Fluidization of bed during transfer could result in a layer of cation resin at the bottom of the mixed bed.	Cation, anion, cation layered (or separate) beds provide sufficient purity for fossil power plants. Regeneration is simpler than for mixed beds since resins are already separated. Additional rinsing and soaking of trail cation resin may be used to minimize sulfate.	Sulfate and sulfonate leakage from trail cation layer (bed) may be a concern for some plants. For these plants, “dipole” (cation/anion) may be considered. Note: mixed beds may suffer from the same problem if not maintained in a fully mixed condition.
Operation during condenser in-leakage	Kinetic performance dependent on condition of resin and bed depth, but theoretically should provide best performance.	Proximity of cation to anion resin may increase rate of anion resin fouling.	Kinetic performance similar to mixed bed. Anion resin may foul less. Separate bed design can also provide greater bed depth	Sulfate from trail cation. Layered bed has similar depth to mixed bed. Higher flow rates may have impact although power plant experience has typically been good.
Automation/ manpower		Complete regeneration automation difficult. Ammonia form operation requires well trained operators.	Regeneration more easily automated than mixed bed regeneration.	Some regeneration steps should at least be validated by operational or chemistry personnel.
Cost	Naked mixed bed typically has lowest capital cost	Operational costs for mixed bed higher than for layered or separate bed design.	Capital cost for layered bed design similar to mixed bed. Higher flow may allow fewer service vessels.	Higher capital cost for separate bed design.

2.6.4 Two Stage Separate Bed Polishing Plant Designs

The success achieved by several very large power stations in operating separate deep bed polishers consisting of simply a cation exchange stage followed by an anion exchange stage is interesting. Reports from one station claim that this approach further reduces levels of sulfonate derived from cation exchange resins in the final polished water. The benefits of a two stage separated bed system should therefore be investigated. Such studies could easily be made on existing separate bed polishers provided that they are equipped with appropriate sampling facilities. The possibility of further simplifying the layered bed/single vessel system by using only a cation resin and anion resin layer should also be investigated.

2.7 Conclusions

Separate bed condensate polishing plants have been successfully used for many years on different types of fossil power stations with experience on at least one plant dating back to 1982. In view of the experience obtained polishing plants of this general type should be considered when planning the installation of a condensate polisher on a new station or retrofitting an older station. Although the purity of the effluent from separate bed plants as currently designed and used can far exceed the requirements of fossil power stations it will not meet the much higher requirements sought by nuclear power stations.

Experience has been gained on separate bed polishers operating in both the conventional H-OH mode and in the economical ammonium form. Results obtained during prototype trials of a proprietary layered separate bed polisher showed that it was effective in treating influent containing up to 1 mg/kg (ppm) of ionic impurities. There is also evidence that a full scale polisher was effective in protecting a boiler against a massive ingress of impurities during a very large inleakage incident.

The information that is available on the behaviour of the various types of separate bed condensate polishing plant is encouraging with operators viewing them very favourably relative to the use of mixed beds. However, the existing data base is smaller than that for mixed bed polishing plants as they have historically been more widely used on fossil stations and are used on nearly all nuclear plants. Operators of separate bed polishers should therefore be encouraged to share their experiences and views.

Separate beds of ion exchange resins can be applied in condensate polishing plants in two general ways. They are:

- separate deep beds of cation, anion and cation exchange resins used in service vessels of a conventional design with the resins being regenerated either in these vessels or externally. A variant of this approach simply uses a deep bed of cation resin followed by an anion resin bed
- a proprietary design employing relatively shallow layers of cation, anion and cation resins. These layers are held in a single vessel being separated by supporting perforated screens. Regeneration of these resins is carried out in an external plant.

Both the deep bed and the proprietary layered separate bed designs are considered to be easy to use by operators and have other advantages with the former potentially offering greater capacity than a conventional mixed bed polisher and the latter offering economy and saving of space. The ease in which they can be used in the ammonium form, in contrast to the difficulties sometimes faced by operators of mixed bed polishers, is seen as one of their particularly useful features. This will commend them to power stations unable or reluctant to employ off-site regeneration of their polisher resins but still seeking to minimise their use of chemicals and the quantity of chemical waste that arises from on-site regeneration.

2.8 References

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A

STUDIES OF THE TRIPOL^R CONDENSATE POLISHING SYSTEM

A.1 Pilot Plant Tests at Gladstone Power Station, Australia

Following the early small scale studies of the proposed Tripol^R design a 1 m (39 inches) diameter prototype unit was built using Johnson Wedge-wire screen with 0.1mm opening (0.004 inches) to support the individual cation, anion and cation resin layers with the three separate compartments that were effectively formed being contained in a single vessel. The fine screen opening size was chosen to minimise resin migration from layer to layer. The depths of resins used were 350 mm (14 inches) in the lead and trail cation resin layers and 500 mm (19.5 inches) in the intermediate anion resin layer. External regeneration of the resins was adopted with, on the prototype, a common cation resin regeneration vessel being used for the lead and trail cation resins and a separate anion resin regeneration vessel. Figure A-1

The prototype was installed and tested at Gladstone Power Station of the former Queensland Electricity Generating Board, a seaboard 6x275 MW plant using drum boilers. The paper by Renouf and Smith describes the installation and use of this prototype under full power station condition and using condensate taken from one of the units [1]. The prototype was operated at a linear velocity of 200 m/h (83 gpm/ft^2) with the resins being tested both in the conventional H-OH state and under ammonium form conditions. The results showed it was capable of yielding polished water in which sodium had been reduced to an acceptable level for fossil power stations in the face of simulated seawater leaks. In this work attention was mainly paid to the behaviour of sodium as this impurity was, historically, the one of most concern when operating polishing plants in the ammonium mode. Analyses for chloride and sulfate were not carried out but, under simulated leak conditions when operating in the ammonium form, cation conductivities of polished water varied from 0.064 to 0.095 μS/cm.

A.2 Pilot Plant Tests at Vales Point Power Station, Australia

Further tests employing the same prototype Tripol vessel as used at Gladstone were carried at Vales Point A power station (then operated by the Electricity Commission of New South Wales). No results from these tests are available.

A.3 Pilot Plant Tests Drakelow Power Station, CEGB, UK

Following the trials in Australia, tests using a similar design and size of prototype vessel were carried out on a 350 MW coal fired once-through unit at Drakelow Power Station operated by the former CEGB in the UK. At the time the tests were carried out impurity levels in the condensate and feed water to this once through unit were being controlled below 2 µg/kg (ppb) sodium, chloride and sulfate but condenser leak conditions were simulated by adding impurities.

A depth of 0.35 m (13.8 inches) of cation resin in the lead and trail position was used with the central anion resin bed having a depth of 0.45 m (17.7 inches). It is reported that delays of several months arose during commissioning owing to unexpected cross-contamination of the resins and inability of the plant to achieve its designed flow rate. Resins from the lead cation bed "entered the anion bed owing to imperfect seals between the wire support screens and the wall of the service vessel …resin also leaked past the seals in the trail cation bed". These problems were overcome. Subsequent observations showed that resin transfer from the Tripol vessel to the regeneration vessels could be made very efficiently [A2]. The cation resin was regenerated with sulfuric acid with one regeneration vessel being used for both the lead and trail resins. The exhausted acid from the cation resin regeneration stage was then used for sulfating the anion resin to displace chloride before the resin was finally regenerated with sodium hydroxide.

The effectiveness of the Tripol plant for condensate polishing was tested, at a linear flow velocity of 210 m/h (85.7 gpm/ft^2), with resins both in the H-OH form and in the ammonium form at pH 9.6. Under H-OH form operating conditions, and in the absence of influent contamination other than the traces already present in the condensate, leakages of 0.1 µg/kg (ppb) sodium and < 0.1 µg/kg (ppb) chloride were measured. The sulfate level was reported as being 0.6 µg/kg (ppb) but it is now believed that analytical procedure in use at this time contributed a high bias of about 0.3 µg/kg (ppb) making the true sulfate leakage to be about 0.3µg/kg (ppb), Figure A-2. When operating in the ammonium form at pH 9.6 and in the absence of simulated impurity in-leakage the sodium leakage increased to about 0.5 µg/kg (ppb). It further increased to about 1 µg/kg (ppb) when the influent was dosed with sodium chloride in a series of tests involving additions of up to 1000 µg/kg (ppb) sodium. Chloride leakage in the influent remained low at about 0.1 µg/kg (ppb), Figure A-3. Sulfate levels in the influent waters used in the various tests was low as its removal behaviour was not one of the main aims of the studies. On one test, under pH 9.2-9.6 ammonium form conditions, an inlet sulfate concentration of 500 µg/kg (ppb) was reduced to approximately 1 µg/kg (ppb) in polished water.

The main emphasis of the Drakelow tests was, as in the earlier trials at Gladstone Power Station, placed on studying the behaviour of sodium. However, measurements were made of the operating capacities shown by the cation resin in the lead cation bed. When running to a 0.1 µS/cm end point, a capacity of 85% of the total capacity of the cation resin was achieved. In these tests 220 grams of sulfuric acid/litre of resin were used for regeneration, a level slightly higher than that more normally used i.e.~ 160 g sulfuric acid/litre of resin. There is experience that indicates that this higher level of acid could be expected to increase operational capacities, from about 50% to 60% of the total capacity. It was suggested by the CEGB staff carrying out the Drakelow tests that the even distribution of resin and the better flow distribution achieved on the Tripol^R were important in obtaining the 85% operating capacity. It must be noted that the high cation resin capacity seen is all the more interesting as it was obtained using flow velocities of 210 m/h (85.7 gpm/ft^3), in contrast to the 120 m/h (49 gpm/ft^3) used on most mixed beds [3]. The concentrations of chloride and sulfate in the polished water were also measured during these tests

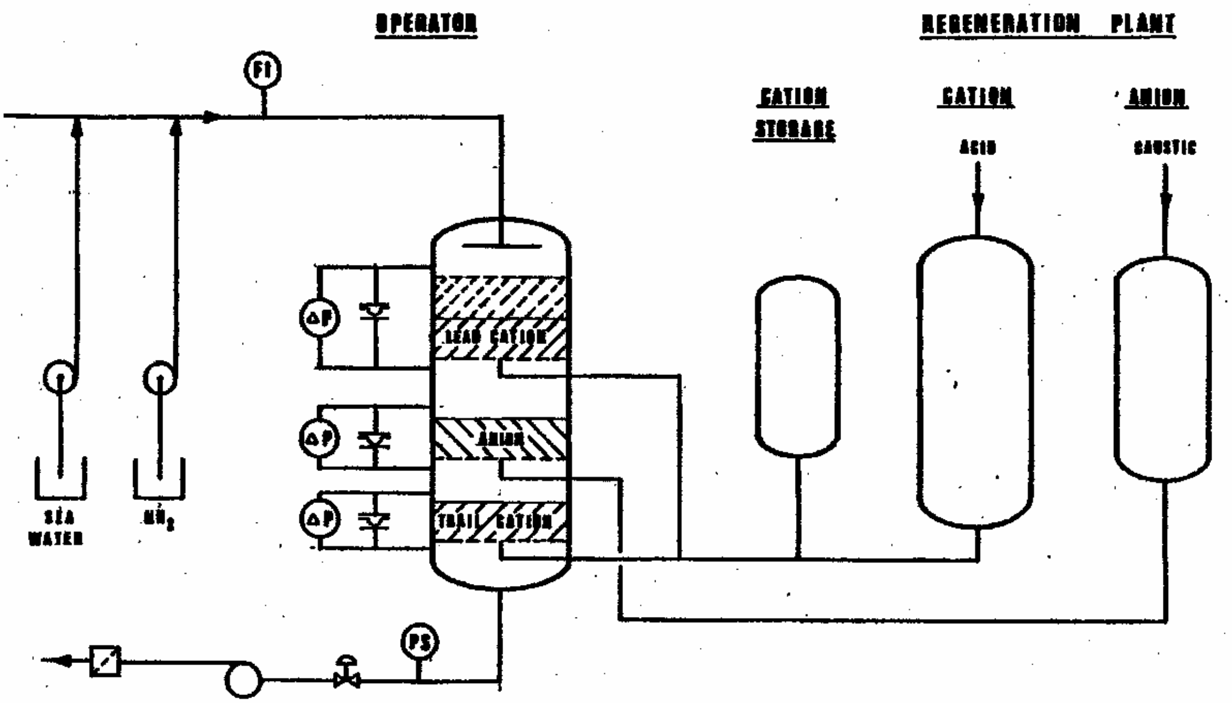

Figure A-1
Tripol^{R} Condensate Polishing Plant Layout, Renouf and Smith. 1981

Source: P.W. Renouf and J.H. Smith, IWC-81-20, 42nd Annual Meeting of the International Water Conference

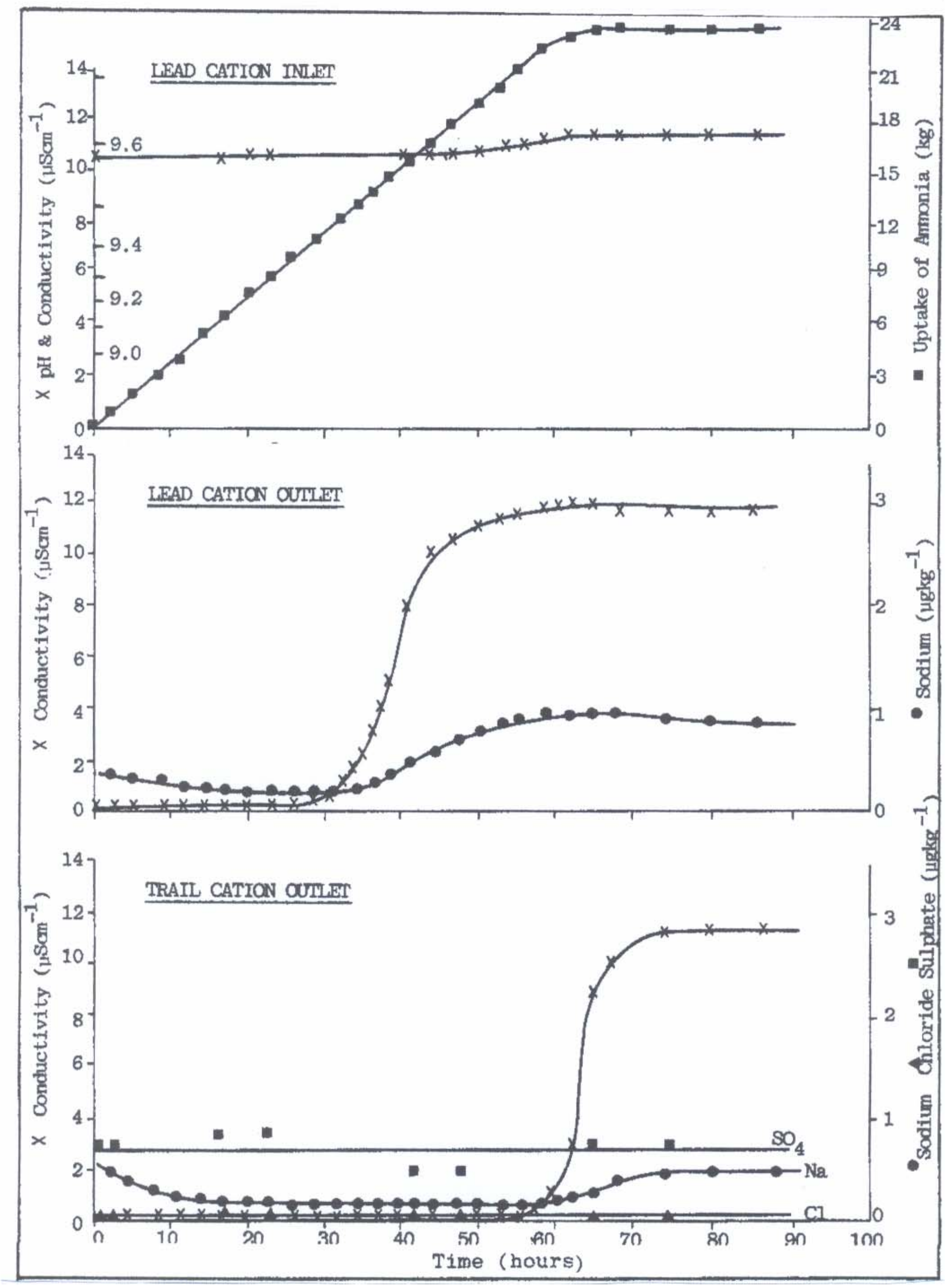

Figure A-2
Hydrogen Form Operation of Tripol to Ammonia Breakthrough at pH 9.6 Using Gel Cation and Anion Resins and Operating On a Condensate Without Simulated Condenser Leaks.
Source, Ion Exchange Technology, D. Naden and M. Streat, Ellis Horwood, 1984

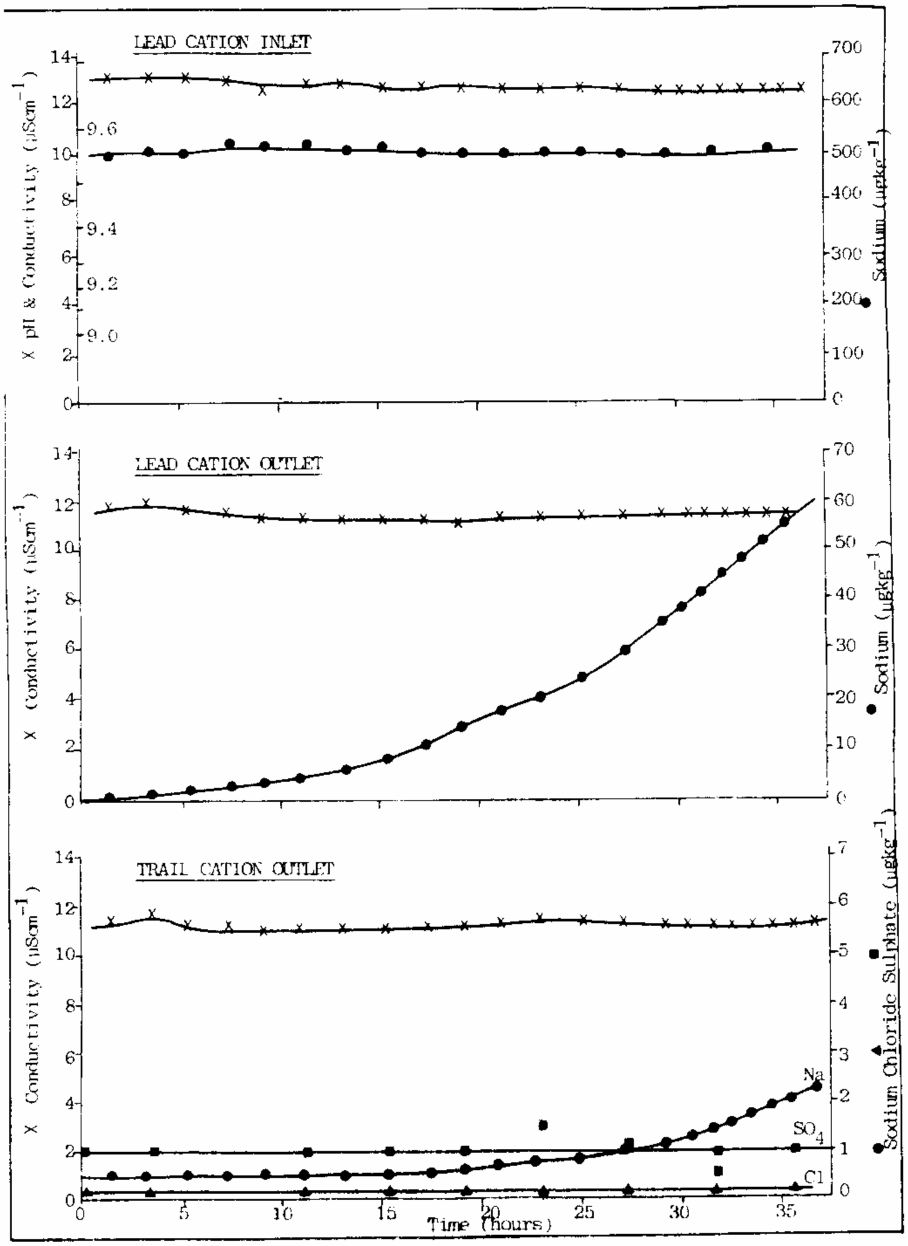

Figure A-3
Ammonium Form Operation of Tripol at pH 9.6 With Simulated Condenser Leak (500 ppb Sodium)

Source: Ion Exchange Technology, D. Naden and M. Streat, Ellis Horwood, 1984

A.4 EPRI Sponsored Pilot Plant Tests of the Proprietary Tripol^R Layered Separate Bed Condensate Polishing System by Southern California Edison, USA

A.4.1 Introduction and Background

In 1987, Southern California Edison (SCE) operated two nuclear units and eight supercritical once-through fossil-fueled generating units that utilized full in-stream deep-bed condensate polishing. In addition, SCE operated two 1960 vintage sub-critical once-through units with side-stream deep-bed condensate polishers and precoat filters. The polishers at this location were the first condensate polishers installed on the West coast of the U. S. while the polishers at units 2 and 3 at San Onofre Nuclear Generating Station (SONGS) were a recently installed state-of-the-art cation/mixed-bed design [4].

Years of resin testing and polisher design review preceded the retrofit of the cation/mixed-bed condensate polisher systems at San Onofre units 2 and 3 that combined mixed bed and separate bed design. This work included special attention being devoted to the ultra-trace leakage of sulfonate and sulfate that involved the development of innovative analytical techniques. To overcome the problems associated with cross-regenerant contamination of mixed-bed polisher resin experienced at fossil plants, the regeneration system at SONGS included a special separation vessel and interface tank that optimized hydraulic separation and transfer of the separated mixed bed resins as much as possible. However, for fossil plants considering the retrofit of condensate polishers, the SONGS design was too expensive and still required dedicated operators to assure good mixed-bed resin separation. Consequently, the use of separate bed polishing became an attractive and potentially viable option to explore for future polisher installations.

A.4.2 Experimental Program and Results

In September of 1987, the Electric Power Research Institute (EPRI) contracted with SCE to test and evaluate the performance of a proprietary layered separate bed polishing configuration called Tripol. (See Figure 1-5 for system layout and regeneration system configuration.) Although the project's primary objective was to determine if this approach to separate bed polishing could consistently meet effluent limits of 50 ng/kg (ppt) sodium, chloride, and sulfate, a number of other important areas were also investigated. A summary of some of these key areas is provided in the list that follows.

- Impact of separate bed polishing on anion and cation exchange kinetics (during simulated leak tests using different flow rates, various levels of influent contamination, and different cation resins)
- Effect of temperature and regenerants on the level of resin extractables and ionic leakage
- Extent and impact of cross contamination resulting from migration of resin fines across the wedgewire screens

- Comparison of weak and strong acid cation resin with respect to ionic leakage (especially sodium and sulfate), resin extractables, pressure drop, rinse down characteristics, exchange kinetics during a simulated leak, and any other differences observed
- Effects of flow rate, "stand" time, ammonia rinse of the anion resin after caustic regeneration and deionized water rinse, and intentional contamination of the cation resin with measured quantities of anion resin on "rinse out" of regenerants
- Effects of atypical cation resin regenerants (e.g., citric and nitric acids) on sulfate and regenerant rinse out from both weak acid and strong acid cation resins
- And the performance of various instruments used for on-line monitoring

In addition to the typical on-line instruments such as conductivity and TOC, a laboratory ion chromatograph was adapted for on-line determination of monovalent cations, inorganic anions and organic chlorides and sulfonates using UV oxidation. Scanivalves with Teflon on all wetted surfaces were customized to be used as stream selectors. They were controlled through the same computer that automated the on-line IC through a programmed sequence of analyses. Chromatograms and other data were also printed out to allow for further review. In addition to the operation of on-line analyzers, grab samples were collected in triplicate during each critical test period and subsequently analyzed at SCE's central laboratory. Although some of the results obtained were unexpected, there is a high degree of confidence in the values because of the validation techniques employed.

The vessel was supplied skid mounted and installed at Huntingdon Beach Generating Station by a US manufacturer. It had a diameter of 1.07 m (3.5 ft) with the resin compartments being separated by wedge-wire screens with openings of 0.1-0.15 mm (0.004-0.006 inches or 115 mesh). The lead cation layer was designed to have a depth of 0.279 m (11 inches), the anion resin layer to be 0.406 m (16 inches) deep and the secondary or trail cation layer to be 0.279 m (11 inches) deep. It is to be noted that the depth of resin used in the SCE tests in both the cation compartments of the Tripol^R and also in the anion compartment is less that used in the CEGB, Drakelow, tests. The minimum design velocity was 147 m/h (60 gpm/ft^2) and the maximum 208 m/h (85 gpm/ft^2). Separate regeneration vessels were provided for the external regeneration of the lead and trail cation resins and also for the anion resin.

In order to be able to operate the prototype layered separate bed polisher at will without adversely impacting an operating unit or waiting for a unit to be on line, a plant location with two large tanks was selected. These tanks were associated with operation of two units at SCE's Huntington Beach Generating Station. One of the tanks was called a "bitters" tank because it received makeup water and condensate that could be polished and sent to the unit or to a "sweet water" tank. Since the polishers on these units were only capable of one third full flow, they were used in a partial polishing mode during normal service and typically at full flow during startup of a unit.

The use of both the "bitters" tank and the "sweet water" tank for the testing of the prototype layered separate bed polisher was initially considered. However, since the discharge from the "sweet water" tank was sent directly to a unit, it was decided to use only the "bitters" tank for the testing to avoid possible contamination of the unit and competition for influent water. Consequently, the "bitters" tank supplied the influent to the Tripol^R at the same time it also received its effluent and inconsistent quality makeup water (the effluent quality limits for the makeup demineralizer for these units were less stringent than they were at other SCE stations because all makeup water was "polished" by being sent through the condensate polishers). It should also be noted that during unit startup the bitters tank received condensate with corrosion products. Although analysis of the polisher influent (bitters tank) was always included in the testing protocol, it is important to recognize that undetected organics from the makeup demineralizer could have periodically been present since even the on-line sampling was not continuous. Sample collection was cycled through all of the sample sites using the Scanivalve stream selector.

Results obtained by SCE are discussed both in the EPRI report and in a paper subsequently given at the International Water Conference [5,6]. They show that operation in the H-OH mode with slightly contaminated water from a "bitters tank" (i.e. with sodium, chloride and sulfate impurity levels of about 1.5, 0.42 and 0.13 μg/kg (ppb) respectively in the water) gave a polished water of acceptable quality for fossil power stations with sodium, chloride and sulfate levels being less than 0.05 μg/kg (ppb) as shown by Figures A-4, A-5 & A-6. A very small increase of sulfate across the trail cation bed was shown, i.e. ~ 0.06 μg/kg (ppb) but no evidence was found of sulfonate pick-up. Simulated condenser leak tests were performed when operating in the H-OH form. With ammonia levels in the influent being maintained low at about 1 . μg/kg (ppb), the sodium, chloride, and sulfate influent levels were increased to approximately 300, 500 and 80 μg/kg (ppb) respectively. This had little effect on the sodium and chloride leakage but the sulfate leakage increased to approximately 0.6 μg/kg (ppb). Of this leakage about 0.4 μg/kg (ppb) was due to leakage from the anion resin. Increasing the impurity levels in the influent condensate to approximately, 500, 1000 and 140 μg/kg (ppb) of sodium, chloride and sulfate respectively resulted in the sulfate leakage increasing to1.6 μg/kg (ppb).

All this work was carried out at a flow of 136 m^3/h (599 gpm) that was increased to 182 m^3/h (802 gpm), i.e. from a linear velocity of 173 m/h to 232 m/h (70.6-94.7 gpm/ft^2). It was observed that sulfate leakage from both the anion layer and from the trail cation bed increased to 1.7 and 3.1 μg/kg (ppb) respectively when the flow was increased. Most of the increase can therefore be seen as arising from increased leakage of sulfate from the anion resin bed. In all these tests the leakage of chloride remained low, i.e. <0.05 μg/kg (ppb).

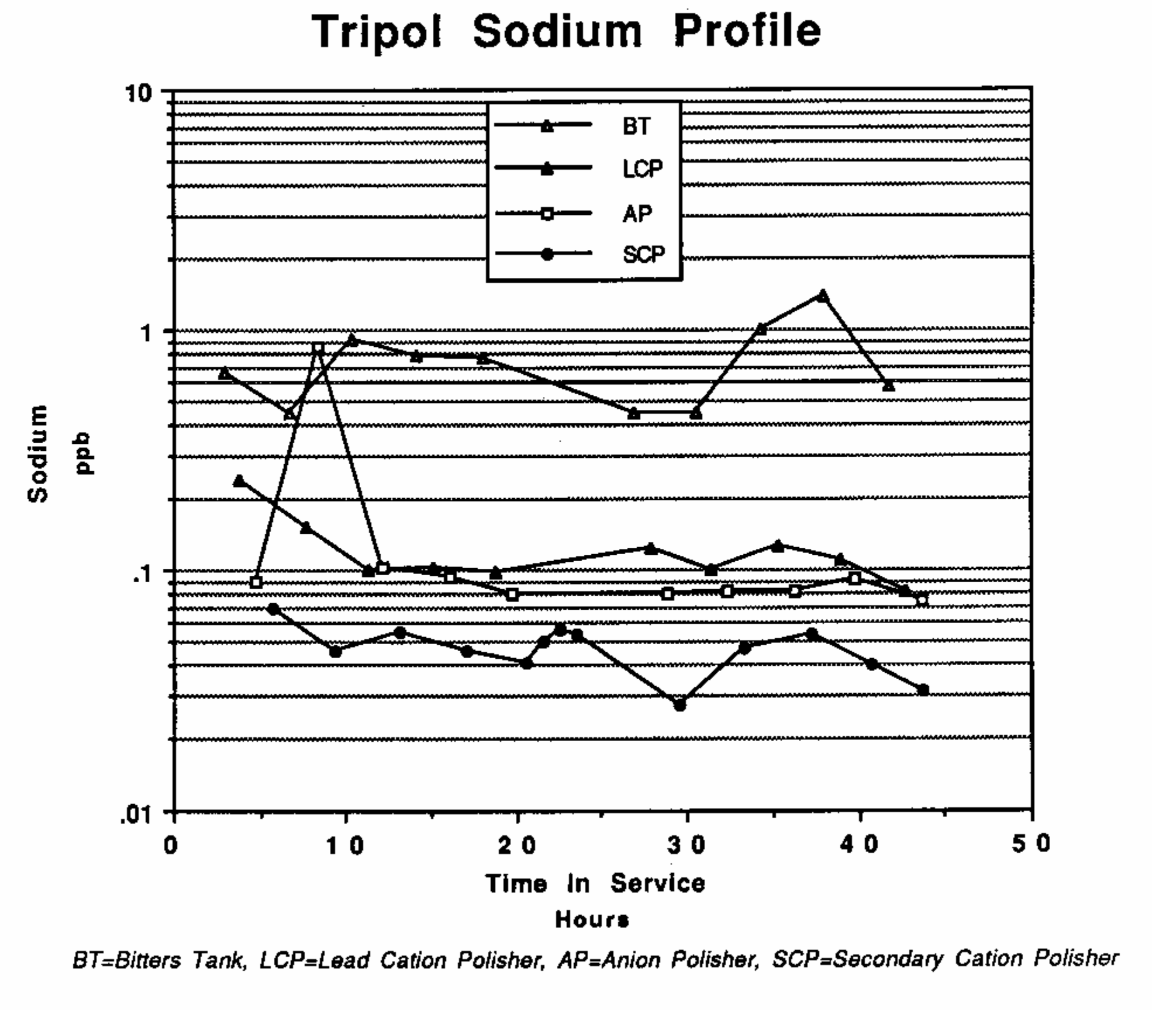

Figure A-4
Sodium Levels in Condensate at Stages Through the SCE Prototype Tripol Vessel Operating in the H-OH Mode

Source: D.C. Auerswald, F.M. Cutler, and S.S. Simmons, IWC-89-37

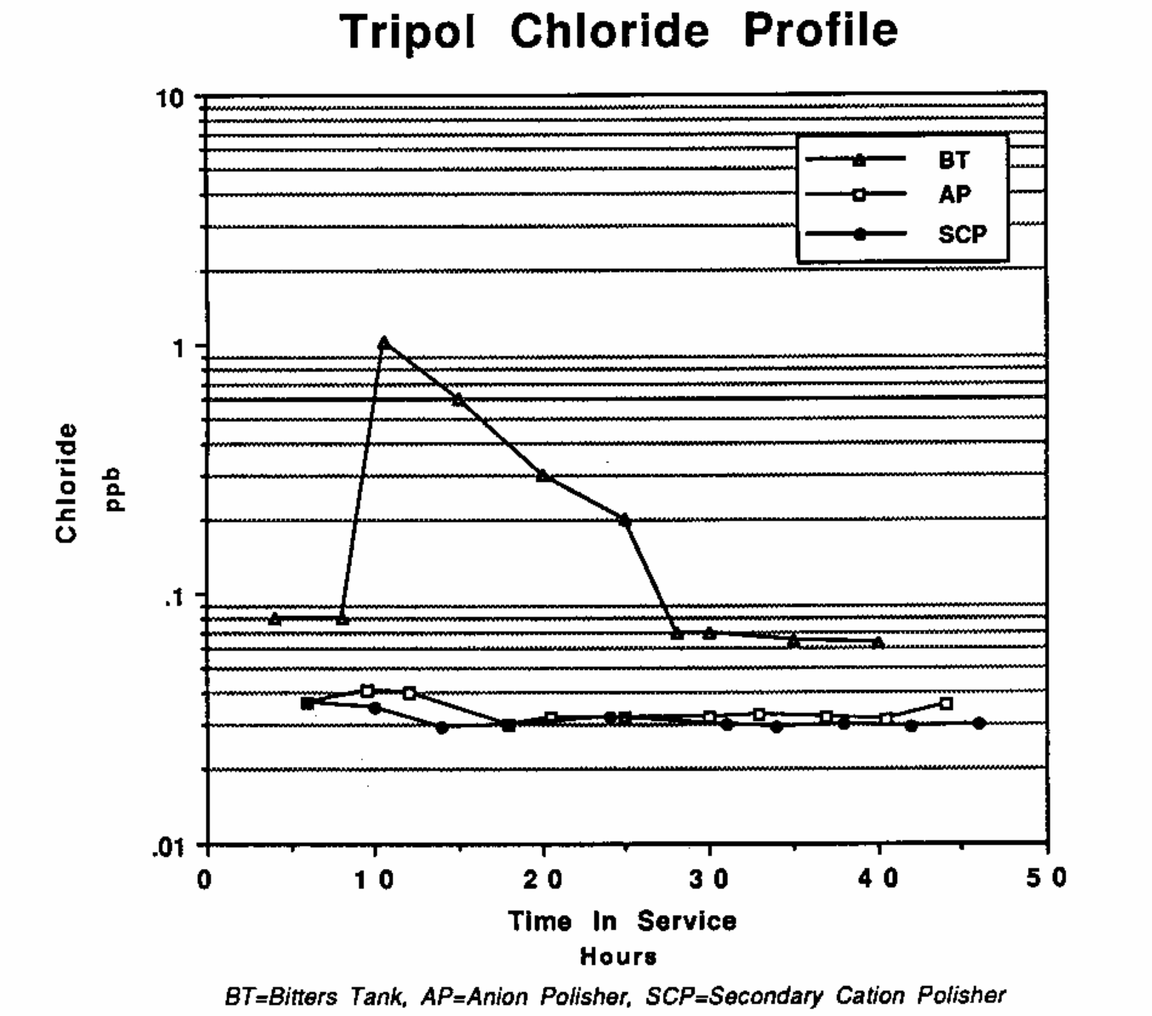

Figure A-5
Chloride Levels in Condensate at Stages Through the SCE Prototype Tripol^R Vessel Operating in the H-OH Mode

Source: D.C. Auerswald, F.M. Cutler, and S.S. Simmons, IWC-89-37

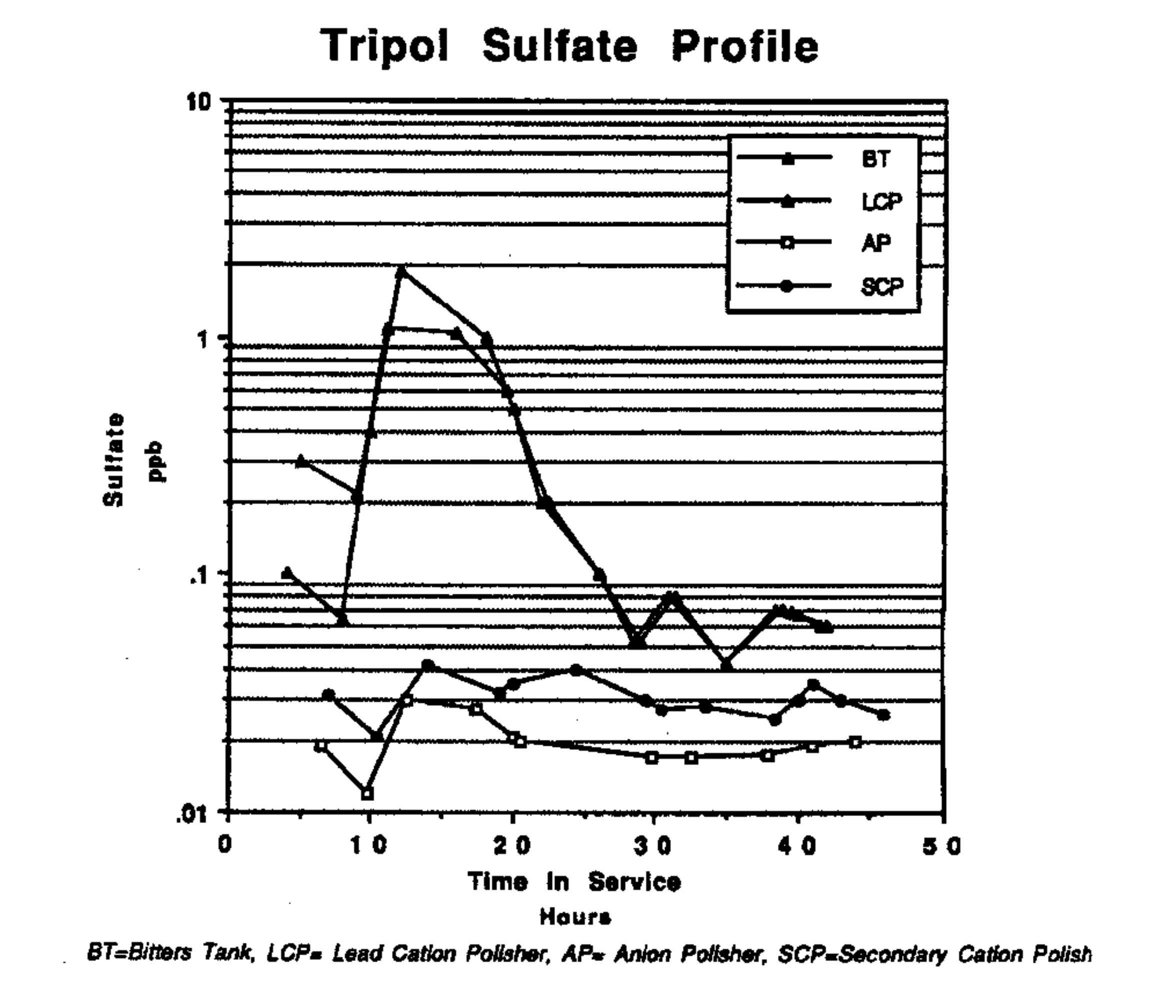

Figure A-6
Sulfate Levels in Condensate at Stages Through the SCE Prototype Tripol^{R} Vessel Operating in the H-OH Mode.

Source: D.C. Auerswald, F.M. Cutler, and S.S. Simmons, IWC-89-37

Thus, under H-OH conditions, sodium and chloride impurities in simulated leaks were effectively held but the sulfate leakage increased being both flow and concentration sensitive. For some reason the behaviour of the anion resin in removing sulfate was obviously not as effective as its action in removing chloride as maximum leakages of about 1.7 µg/kg (ppb) sulfate were seen under high sulfate input and high flow conditions. The contribution of the trail cation resin varied from about 0.4 to1.4 µg/kg (ppb) depending on influent conditions and the rate of flow.

When operating in the ammonium form at pH 9.5 under “no inleakage” conditions (i.e., with a sulfate input of only 28 µg/kg (ppb)) a leakage 0.48 µg/kg (ppb) sulfate from the anion resin was measured and this increased to 3.7 µg/kg (ppb) over the trail cation bed. Other tests involving simulated condenser leaks used influent sulfate levels ranging from 28 to 205 µg/kg (ppb) and resulted in the sulfate leakage increasing significantly with a maximum being 13 µg/kg (ppb). Again, the main source was the trail cation resin. Finally, the sodium input levels were increased to 660 µg/kg (ppb) resulting in sodium levels in water from the trail cation increasing to 6 µg/kg (ppb). These high leakage figures are believed to be due to the cation resins having been incompletely regenerated. A sodium content of about 0.5% would explain the sodium leakages seen. Chloride levels remained low with final polished water levels of about 0.2 µg/kg (ppb). This level is similar to that observed by stations operating mixed beds in the ammonium form at the same pH.

On the evidence of the SCE/EPRI tests, the polishing behaviour of the Tripol when operating in the ammonium form appears unacceptable for nuclear or most high pressure fossil boilers. In particular, the high sulfate leakages encountered when the plant was being challenged by simulated seawater in-leakage were of concern. It must be pointed out, however, that during the earlier prototype trials at Drakelow, ammonium form resins operating at both pH 9.2 and 9.6 were challenged with ammonium sulfate solutions containing up to 500 µg/kg (ppb) sulfate without a marked increase in the leakage of this impurity.

The prototype layered separate bed polisher exhibited excellent performance with respect to chloride and sodium removal during both normal operation and leak tests. The only significant question about its performance raised by the SCE study was related to sulfate leakage from the trail cation resin during leak tests. The behaviour observed during the SCE work was not seen during the previous prototype trials at Dakelow nor has it been reported from any of the full scale layered separate bed polishers some of which have now been in station service for over 20 years. The effect seen by SCE researchers showing high sulfate leakage from the trail cation resin when treating contaminated condensate under ammonium form conditions therefore remains unexplained although several explanations have been suggested. Further work focused on sulfate release by resins was carried out by SCE and is summarized below.

A.4.3 Resin Studies Employing Weak Acid Cation Resins as an Aid to Understanding Leakage of Sulfate from Strong Acid Cation Resins as Seen On the Prototype Tripol^R Polisher

The use of weak acid cation resin to eliminate the potentially significant source of sulfate in strong acid cation resin appeared to be an attractive option to explore for selected polishing applications. However, field testing of weak acid cation resin is only practical in a separate bed configuration because of its swelling characteristics. Thus the prototype separate bed polisher tests offered a rare opportunity for large scale testing of the benefits, if any, of using this type of cation resin in condensate polishing. The bottom line from a performance perspective is that sodium removal with weak acid cation resin in the hydrogen form is not good enough for its use in the trail bed of a separate bed polishing plant.

Laboratory tests with ammonium form weak acid cation resin showed some improvements, but still did not achieve desired purity results. In addition, the use of weak acid cation resin does not automatically eliminate sulfate as a contaminant. Although weak acid cation resins should not have any sulfate components, they are not all alike. Discussions with resin manufacturers indicated that there are different methods of manufacturing weak acid cation resin, some of which utilize sulfuric acid. All new weak acid cation resins have to be thoroughly conditioned before use because of residual manufacturing impurities. In fact, some weak acid cation resins also contain sulfate in their structure as part of their manufacturing. It was also shown that sulfuric acid regeneration of weak acid cation resins could produce sulfate sites on the resins.

The most noteworthy data from the testing of weak acid cation resin comes from the leak test studies using both sulfuric acid and citric acid regenerated weak acid cation resin. Prior to the leak test with sulfuric acid regenerated weak acid cation resin, the resin was soaked in hot water at a temperature of 43-54 °C (110-130 °F) for 75 minutes and then exhausted to the ammonium form. The resin was then regenerated with sulfuric acid and put back into service in preparation for simulated leak tests. With influent levels to the polisher unit of 670 µg/kg (ppb) chloride and 90 µg/kg (ppb) sulfate, there was no measurable increase in chloride or sulfate detected across the trail cation bed containing weak acid cation resin at any time during the test. While this sounds like good news, the sodium removal was even poorer than expected throughout the test making the use of weak acid cation resin unnecessary since it appears to be unable to perform its primary function of sodium removal.

A leak test with citric acid regenerated weak acid cation resin in the trail bed was undertaken following replacement of the anion resin and sulfuric acid regeneration of the strong acid cation resin in the lead cation polisher. Although the results for chloride removal across the polisher were similar to the prior leak test with sulfuric acid regenerated weak acid cation resin, there was improved sodium removal and a small sulfate pickup across the trail cation bed containing weak acid cation resin. Taken together, these results suggest that some strong acid sites, possibly introduced on to the weak acid cation resin during prior sulfuric acid regeneration, were available and resulted in improved sodium removal. Why these notional "strong acid" sites might be more available after citric acid regeneration is a question for the resin manufacturers. Another question for them is whether these sites might also be more subject to displacement after citric acid regeneration leading to the pickup in sulfate shown during the leak test. How citrate (or other organics such as ethanolamine or those present in makeup water effluent) may be involved in triggering these effects needs to be pursued.

The results of the Tripol tests reported by SCE are, however, supported by additional laboratory testing using cation columns similar to those used in most power plants. The original function of these columns was to remove ammonia from high pH samples collected for trace anion analysis by ion chromatography. However, there was some concern about the sulfuric acid regenerated strong acid cation resin contributing to sulfate in the analysis. Consequently, the use of different regenerant acids on both strong acid cation resin and weak acid cation resin was investigated to determine which resin and regenerant provided the least potential for adding contaminant anions. Sulfuric acid, hydrochloric acid, nitric acid, and citric acid were used on the strong acid cation resin. Sulfuric acid, hydrochloric acid, and citric acid were used on the weak acid cation resin.

It was this initial laboratory testing that demonstrated the potential contamination problems with the weak acid cation resin were being considered for use in the trials of the prototype separate layered bed polisher and led to focus being placed on obtaining the cleanest weak acid cation resins available. All of the initially tested weak acid cation resins contributed sulfate and other contamination even after conditioning. The two cleanest weak acid cation resins subsequently obtained showed the same pattern of sulfate throw observed during the leak tests carried out on the prototype polisher, i.e. initial sulfuric acid regeneration followed by regeneration with citric acid resulted in a measurable pickup of sulfate during leak type conditions. Even more interesting than the results with weak acid cation resin are the results of testing different regenerants on strong acid cation resin.

Strong acid cation resin regenerated with either sulfuric acid or hydrochloric acid and appropriately rinsed to remove regenerant acid showed the same small sulfate increase during simulated leak testing. A pickup of sulfate has also been reported by the Japanese who use hydrochloric acid to regenerate the cation resin indicating that something other than the regenerant contributes to sulfate out of a strong acid cation resin. Resin that was also allowed a 24-hour stand period after being rinsed down showed a smaller pickup. The nitric acid regenerated strong acid cation resin had a smaller sulfate pickup and this could possibly be attributed to the fact it was used at a lower strength (2%) than used for hydrochloric acid and sulfuric acid. The nitric acid was found to affect the dye on the cation resin used to indicate column exhaustion. It is stressed that use of nitric acid is not suggested or even considered for general plant use at any concentration.

A.4.4 Summary and Conclusions of Tests of Prototype Tripol^R Condensate Polishing System by SCE

A major goal for SCE in undertaking the Tripol^R testing was to determine if the separate bed configuration eliminated the problems associated with separating mixed bed resin prior to regeneration without creating new or different problems. With the exception of not resolving the issue of sulfate pickup across the trail cation resin bed during simulated leak testing, this separate bed configuration appears to offer a simple and viable option for condensate polishing in fossil plants. The results from this investigation, combined with experience in the use of mixed bed and cation/mixed bed condensate polishing plants, indicate that the layered separate bed configuration is capable of producing condensate of a purity that satisfies fossil plant quality requirements. It may also be possible for the configuration to be satisfactorily used at nuclear plants if the trail cation bed is replaced with a small, disposable layer of mixed bed resin.

Laboratory tests also indicated that the exchange kinetics of the anion resin used in the Tripol separate bed configuration was similar to the exchange kinetics of anion resin in a well-performing mixed bed polisher. One very positive impact of separate bed polishing on anion exchange kinetics results from the lead cation bed acting as a filter to remove a good deal of the influent corrosion products. A similar situation was observed with the polisher resin at Huntington Beach that was protected by pre-filters.

Much has been said about cation resin regenerants and their impact on subsequent cation resin performance. For the trail cation resin in the prototype layered separate bed configuration, using a lower concentration of sulfuric acid for regeneration along with extended rinse and stand time might be beneficial for reducing subsequent sulfate throw. With the exception of corrosion product removal, there does not appear to be a significant benefit in using hydrochloric acid for regeneration unless it is the acid of choice for other applications (e. g., makeup demineralizer regeneration). There could be disadvantages particularly if the resins were used in the ammonium form.

During the limited duration of the tests, cross contamination resulting from migration of resin fines across the wedgewire screens was not observed. In fact, for one test, anion resin was purposely added to the cation resin in the trail bed to determine what the increase in sulfate rinse out and leakage would be. Although rinse down took somewhat longer, the effect of adding different amounts of anion resin resulted in a small but similar increase in effluent sulfate. This behaviour conforms with that expected from theoretical considerations.

Comparison of weak and strong acid cation resin in the trail cation bed of this prototype layered separate bed plant with respect to ionic leakage indicates that weak acid cation resin is not useful because of its limited sodium removal capability. Although some tests with weak acid cation resin showed no pick up in sulfate across the bed, a change in operation could easily alter that result. Also, extreme care has to be taken in rinsing and preparing the weak acid cation resin. Consequently, the use of weak acid cation resin in the SCP does not appear to provide any appreciable benefit.

Ammonia rinse of the anion resin after caustic regeneration and appropriate displacement and fast rinses with deionized water does reduce sodium throw from the anion resin. The time needed to complete the ammonia rinse varies with the amount of cation resin cross contamination. For the Tripol^R configuration where the anion resin should not be contaminated with cation resin, the ammonia rinse time should be on the order of an hour or two. The need to cleanse ion exchange resins of traces of the chemicals used for their regeneration is becoming important and is mentioned in the main report. Other methods of cleansing have been suggested and some are already in use.

Regeneration of the resins during testing at SCE was carried out on site using a separate regeneration vessel for each of the three resin layers. The lead and trail cation resins were not mixed for regeneration. This is the recommended arrangement to avoid contamination of the trail cation resin with corrosion products from the lead cation bed. It is always best to have the most highly regenerated resin the last contact for the polished water especially since corrosion products may be a significant source of sulfate.

The unusual sulfate behaviour across the trail cation resin remains unexplained. It is extremely unlikely that the results were affected by analytical problems and errors as the researchers involved were both experienced and knowledgeable. The effects reported were not seen on the earlier studies on an almost identical prototype Tripol^R system used in the tests carried out by the CEGB at Drakelow nor have they been reported by power stations using polishers of this design. It is suggested that the effects noted were either caused by the batch/type of resins being used, although it must be stressed that there is not any direct evidence of this, or, more likely, from unidentified contaminants in the "bitters tank" water used to supply the rig. The sulfate release behaviour observed during the SCE tests on the prototype Tripol should not act to discourage the use of this design of polisher on fossil power stations. It is nevertheless prudent to continue to look at the experiences of those plants already in service to gain confidence that sulfate leakage does not represent a problem.

A.5 Field Operating Experience: The Behaviour of a Tripol^R Condensate Polishing Plant at Callide C Power Station, Australia During a Large Condenser Leak

Callide C Power Station was commissioned in 2001 and employs Tripol^R condensate polishers to protect each of its 460 MW supercritical boiler. In November 2002 one of Unit 4 experienced a large condenser leak that resulted in the influent conductivity being > 10 µS/cm and both the direct conductivity and the cation conductivity of polished water increasing with peak leakage being about 0.6-0.7 µS/cm. The polishing plant removed approximately 99% of the influent ionic impurities but the polished water conductivity during the incident still exceeded the First Action Limit advised by EPRI and at times it also exceeded Stage 2 Action Limits for "Fossil Power Plants Using Oxygen Treatment". Nevertheless, the polishing plant clearly offered substantial protection and allowed the unit to remain on load without EPRI's "Immediate Shutdown Limits" being breached. The unit was shut down approximately 6 hours after the start of the leak [7,8].

To attempt to interpret the effects of such an inleakage it is necessary to make some basic assumptions as only conductivity data is available. As Callide C employs cooling water from cooling towers it is reasonable to assume that it is conditioned with sulfuric acid and so contains high levels of sodium sulfate. The direct conductivity of the condensate entering the polishing plant went off scale at 10 µS/cm indicating that the water entering the condenser could possibly have contained greater than 6 mg/kg (ppm) of sodium sulfate (approximately 4 ppm sulfate) although it probably contained a mixture of ionic impurities with sodium and sulfate predominating. The cation conductivity of the condensate leaving the polisher during the incident was for 2-3 hours between 0.2 and 0.3 µS/cm peaking at over 0.6 µS/cm. If it is again assumed that the main impurity was sulfate then this would indicate levels of this impurity in the polished water of about 20-30 µg/kg (ppb) peaking at 60 µg/kg (ppb). Figures A-7 and A-8.

If these assumptions give a reasonable view of what occurred it would be useful to know if the behaviour of the polishing plant at Callide can be taken as a guide to what could be seen on other stations or whether it is indicative of a problem, such as kinetically impaired anion resins, being the cause. The experience during a major condenser leak on a 1236 MW PWR in the USA that was equipped with deep mixed bed polishing plant is of interest as there are some similarities to the Callide experiences. Callaway PWR power station uses cooling water drawn from cooling towers that are supplied with make-up from the Missouri river. To provide pH control, sulfuric acid is added to the cooling tower basin. Within minutes of the initial indications of a major leak the steam generator sulfate levels increased to 600 µg/kg (ppb). This behaviour is in contrast to that of chloride and sodium levels in steam generator water that only increased to about 2.1 and 2.7 µg/kg (ppb) respectively. The naked mixed bed condensate polishing plant employs five streams and these showed cation conductivities varying from 0.12 to 0.32 µS/cm indicating the presence of 9 to 35 µg/kg (ppb) sulfate in the polished water. These estimates again assume that the major ionic impurity present was sulfuric acid. Resin tests subsequently showed that the anion resins in all five beds were kinetically impaired with Mass Transfer Coefficients of about 1.2-1.5 m/s x10^{-4} as compared with a value of > 2 m/s x10^{-4} expected from a new resin. The curious difference in the behaviour of the individual mixed beds could not be explained [9].

Strongly basic anion resins are known to be effective in removing of sulfate from condensate both under H-OH and AFO conditions. With sulfate inputs as high as 500 μg/kg (ppb) the prototype layered separate bed polisher on the Drakelow trials gave polished water containing < 1 μg/kg (ppb) when operating at high pH in the ammonium form. More recent tests have been performed at Stanwell in which its full scale polishers were challenged with 380 μg/kg (ppb) of sulfate. These tests again showed that the sulfate was effectively removed by the Tripol plants with polished water sulfate levels not exceeding 1 μg/kg (ppb). The very high inleakage at Callide C obviously presented a far more severe test and some effect on the polished water quality would certainly have been expected. Unfortunately, actual sulfate levels in the influent condensate to the polisher and in the final polished water are not available but some feel for the behaviour of the layered separate beds in use at the time can be obtained by making assumptions. The cation conductivity of the polished water actually seen during the incident indicates sulfate levels of 30 – 60 μg/kg (ppb) in the face of an influent possibly containing levels of sulfate as high as 6000 μg/kg (ppb). There is little information available that will give a guide to the expected behaviour of separate bed polishers when faced with very high impurity ingress incidents. It would be useful to explore their performance under these conditions and to contrast it with that of conventional deep mixed bed polisher. Layered separate bed polishers are used at linear velocities as high as 180 m/h (73.5 gpm/ft^2) and conventional deep mixed bed plants use linear velocities of about 100 to 120 m/h (41-49 gpm/ft^2).

Direct tests to explore the sulfate removal behaviour of polishing plants using high input levels are unlikely to take place on an operating modern power station as the degree of risk of corrosion or deposition is unacceptable. It would, however, be extremely useful to study any data obtained during normal operation under inleakage conditions by stations using polisher of both a conventional design and of the layered separate bed type. It is also suggested that computer modelling of the sulfate exchange behaviour of polishing plant should be carried out examining operation with resins in both the H-OH and ammonium form. Programmes that will allow such studies to be performed already exist.

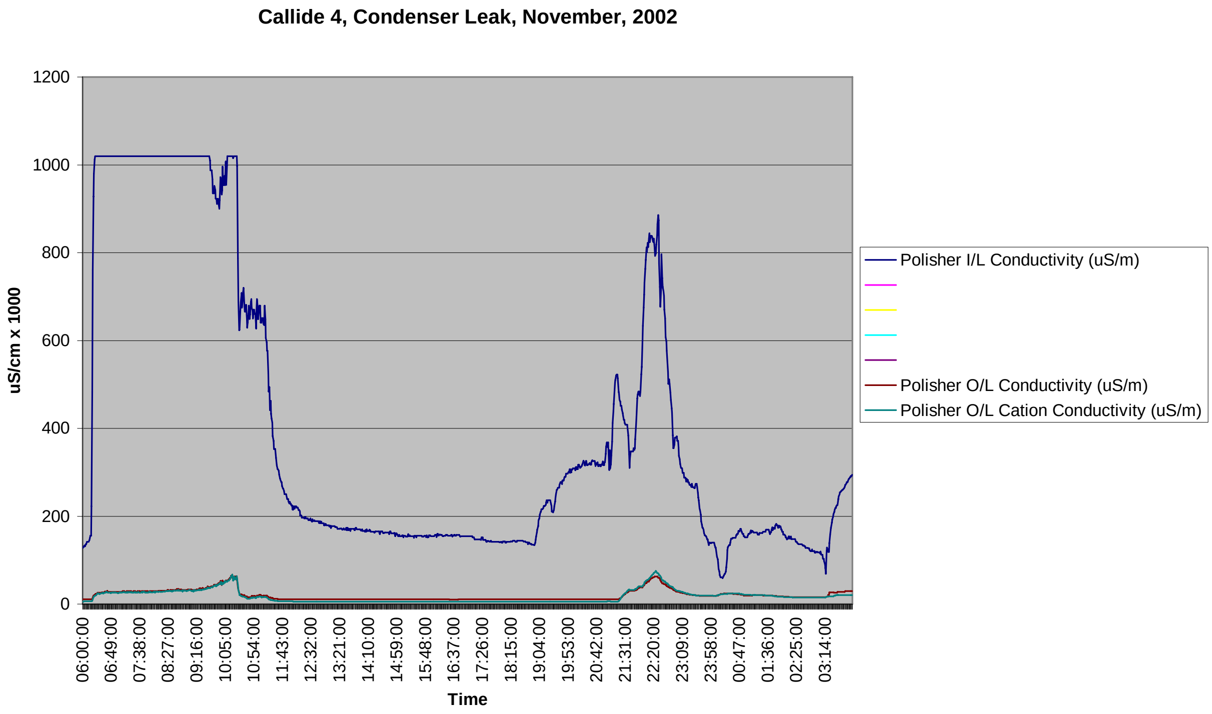

Figure A-7
Conductivity of Inlet Condensate and Polished Water During a Condenser Leak at Callide C Power Station, Unit 4, November 2002

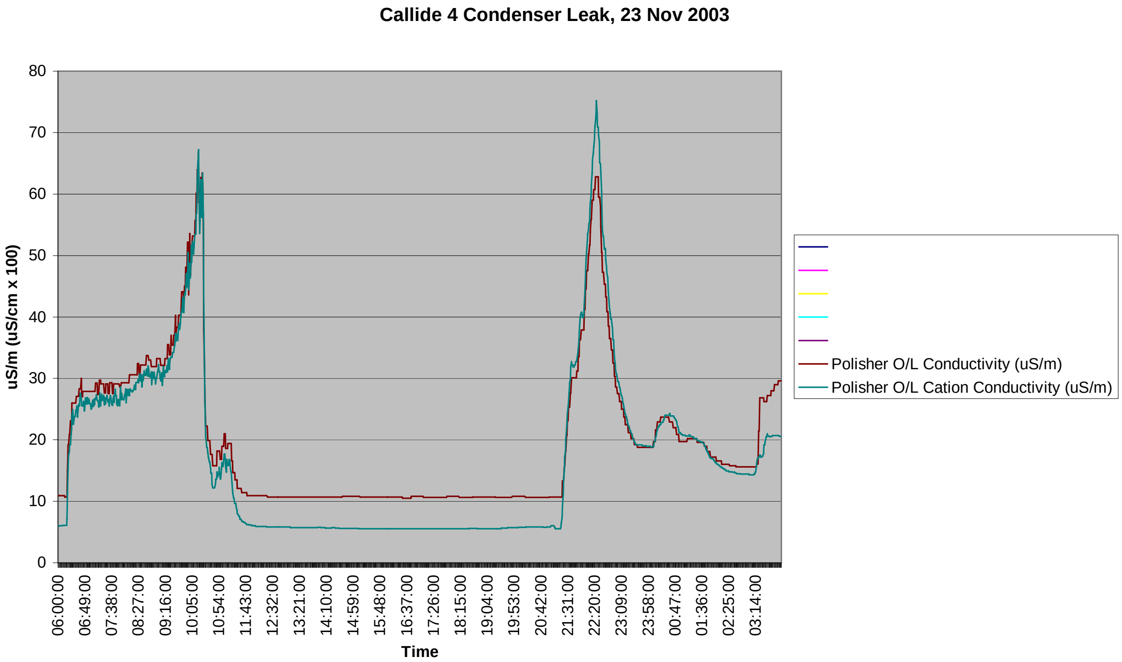

Figure A-8
Conductivity of Polished Water During a Condenser Leak at Callide C Power Station, Unit 4, November 2002

A.6 Miscellaneous Additional Information On Strong Acid Cation Resin and Sulfate Leakage

A.6.1 Effect of Bead Size

Strong acid cation resin with a smaller harmonic mean size showed less sulfate throw during laboratory leak tests than larger sized cation resin of the same type in tests carried out by Southern California Edison. A strongly acidic uniform particle size (UPS) cation resin with a bead size of 650 µm was compared with other UPS resins with bead sizes of 700 and 750 µm. All cation resins were pre-conditioned in the same way. Although the tests were run in duplicate, each resin sample was from a single batch of resin. Additional testing with multiple batches of resin is needed to assure that observed differences were solely due to differences in particle size and not because of batch to batch variations. It is of interest that sulfate pickup across the trail cation bed was seen in the SCE Tripol tests and is described in A5. In these tests the SCP (trail) cation bed) had a harmonic mean size close to 750 µm.

A.6.2 Sulfate Contribution from Corrosion Debris

It has been reported that “sulfate rinse-out from residual iron after H_2SO_4 regeneration is a significant source term ...represents a large and previously under-estimated sulfate source term in any PWR mixed bed that is regenerated with sulfuric acid" [10]. Again this is of interest in relation to the leakage of sulfate seen during the SCE Tripol tests. The "Bitters" tank from which the Tripol was fed was periodically subjected to high levels of corrosion products during the startup of one of the units.

A.6.3 Effect of the Fouling of Cation Resins with Anion Resin Fines and Quarternary Amines

Several tests were performed in an SCE laboratory on strong acid cation resin and indicated that the resin can be fouled with anion resin material. In one test, macroporous anion resin was agitated in a flask for several minutes using a paint shaker-type apparatus. The supernatant liquid was immediately poured over gel cation resin and allowed to sit for about five minutes. The cation resin was then well rinsed, mixed with anion resin, and subjected to kinetics testing. As a control, untreated cation resin was also subjected to kinetics testing. Samples of both "untreated" and "treated" cation resin were paired with both new anion resin and fouled anion resin. The results showed that fouled anion resin paired with "untreated" cation resin exhibited much better anion exchange kinetics than brand new anion resin paired with "treated" cation resin. Quaternary (or tertiary) amines put on the surface of cation resin also appear to cause poor sulfate exchange kinetics in a mixed bed. Another possibility is that some of the anion material put on the surface of the cation resin contained weak base sites.

A.6.4 Oil Fouling of Resins

Another potential source of sulfate contamination to both anion and cation exchange resin in condensate polishers is oil from pumps, compressed air, or lubrication of valves. Resins that become oiled suffer from problems such as poor kinetics and in the case of mixed beds failure to completely separate when required. Thus an enhanced leakage of sulfate becomes a lesser problem as resins either have to be cleaned or replaced On a smaller scale, the original pumps provided with the Dionex ion chromatograph around 1979 to 1980 to concentrate samples for ppb-level analysis were found to contribute sulfate every time a pump was oiled. A type of pump free of the problem was introduced.

An example of one out of three in-service polishers being contaminated with oil occurred at Mohave Generating Station during simulated condenser leak tests on brand new resin. It seems that there was a leak in the effluent line from one of the polishers that required the bed to be depressurized right before the leak testing began. The line was fixed and the in-service leak testing of both hydrogen and ammonium-form polishers was commenced. The resin in the service vessel where the line was repaired had new mixed bed resin with the cation resin in the hydrogen form. One of the mixed beds was approaching ammonium breakthrough while the third bed was fully ammoniated since it had been in service for several weeks at pH 9.5-9.6. The only bed to exhibit poor sulfate exchange kinetics during the simulated leak test was in the vessel that had to be repaired. Traces of oil were found on the resin after it was removed from service.

A summary of potential sources of resin and polisher effluent contamination is provided in Table A-1.

Table A-1
Sources of Resin and Polisher Effluent Contamination

Potential Sources of Contamination from Resin and External Sources	Comments
Sulfuric acid diffusing out of cation resin following regeneration with sulfuric acid	In-service sulfate rinse out following regeneration can be reduced by allowing the resin sufficient stand following initial rinse down to conductivity
Desulfonation of the cation resin	Greater with higher cross-linked resin
Decrosslinking of the cation resin (cation resin oxidative stability)	Moisture content increases; sulfonate extractables may be a problem if decrosslinking is significant
Kinetically impaired polisher resin will result in contaminant leakage during a real or simulated condenser leak	Resin may be fouled by organics from a wide variety of sources including makeup demineralizer or from extractable organics in companion resin
Use of alternate amine for pH control	Problem experienced at many PWRs
Sodium leakage out of ammonium form polisher	Following ammonium break through, equilibrium leakage of sodium from strong acid cation resin is dependent on the amount of sodium left on the cation resin and the operating pH
TOC from anion resin	May foul cation resin and be responsible for decline in mixed-bed kinetics performance
Pump (or other equipment) oil leak	
Breakdown of colloids	
Sulfuric acid regenerant sulfonating resin	Experienced with weak acid cation resin
TOC in influent to polisher	TOC may be removed by polisher and subsequently regenerated off, may foul resin, or pass into system if not removed by the polishers
Sulfate rinse-out from residual iron after sulfuric acid regeneration	

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