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RECENT TRENDS IN CONDENSATE TREATMENT

The paper is a review of the evaluation of treatment processes for obtaining ultrapure water as feeds for high pressure boilers in power plants. It deals mostly with condensate and make-up water.

The approach to the present processes is through presenting after an introduction the three major problems in treating the above waters, namely, fouling of ion exchangers, short runs of the mixed beds and particulates. Then solutions to each of the above are given. Many solution processes are offered for each problem, as an example for overcoming short runs of mixed beds for condensate treatment for processes, the use of highly crosslinked resins, the Ammonex, Calex and Seprex Processes are mentioned.

Existing problems such as temperature stability of anion exchangers, collodial silica, regenerant wastes, fouling of membranes and blowdown wastes are given. However, for each problem, solutions are beginning to appear.

A bibliography of thirty-two paper is presented so readers can consult original sources.

1. INTRODUCTION

As the operating pressure of the boilers in electricity-producing plants increased, the need and demand for better quality feed water, so as to prevent corrosion, deposition and costly shutdowns, also increased. Fig. 1 shows the distribution of salts between water and steam [18] indicating that as the pressure is increased the ratio of the concentration of salts in the vapour to the concentration of salts in the liquid increases. Therefore, to get greater purity of steam with increased pressure, the concentration of salts in the feed water has to be decreased.

Also, with the introduction of the once-through boilers, removal of nearly all solids forming deposit from the feed became a necessity. Four thousand litres of water, containing one milligram of solids per litre if evaporated every minute, would leave a deposit of over 5.5 kg per day. Therefore, rigid specification of water quality are given for boiler feeds, operating at various pressures. Table gives some of the typical specifications [7,

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29]. Figs. 2 and 3 show the points where the water composition is controlled for two types of boilers.

Both the ion-exchanger and the equipment manufacturers have produced ion exchange resins and processes capable of producing such quality waters at reasonable costs. In order to understand the processes deployed, it is essential to be aware of the problems which existed in the 1960's and the approaches developed as solutions in the last 20 years.

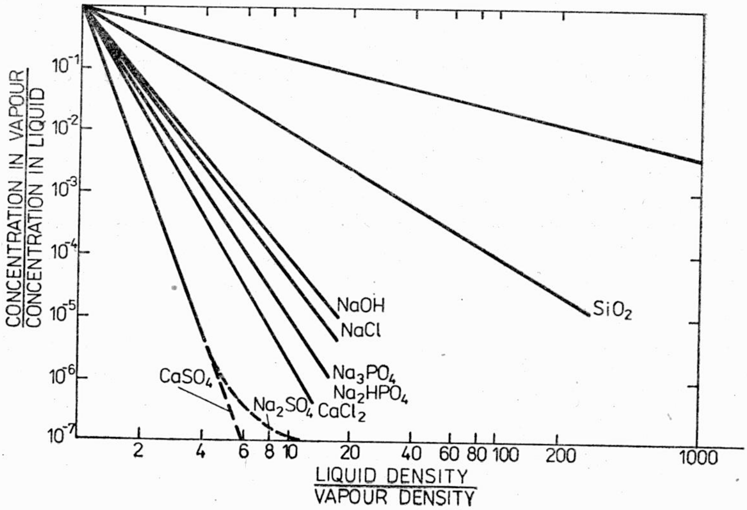

Fig. 1. K_D distribution of solutes between water and steam

Rys. 1. Rozkład K_D substancji rozpuszczonej między wodę i parę

Table

Boiler feed water limits

Dopuszczalna charakterystyka wody zasilającej kocioł

Constituents	Units $\times 10^{-3}$	Type of boiler		
		Drum-type (psig)	Once-through	
		1501–2000	Subcritical	Critical
Total dissolved solids	g/m^3	800	500	50
Hardness	g $CaCO_3$/m^3	10	0	0
Iron	g Fe/m^3	10	10	5
Copper	g Cu/m^3	10	10	5
Silica	g SiO_2/m^3	10	10	10
Oxygen	g O_2/m^3	10	5	5
pH*	—	8.5–9.2	8.8–9.6	8.8–9.6

* Value of pH depends on material of construction.

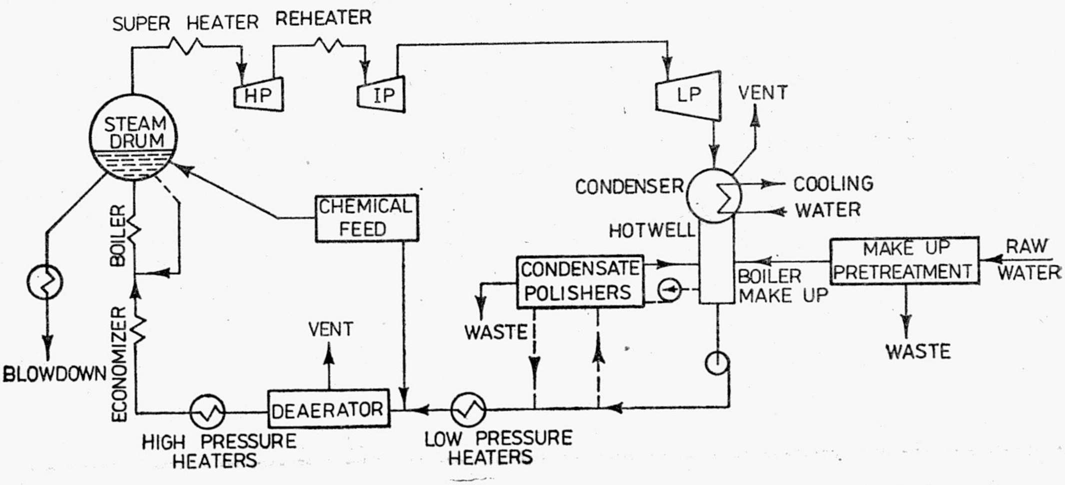

Fig. 2. Methods of controlling boiler water composition in drum-type boilers

Rys. 2. Metody kontrolowania składu wody w kotłach typu bębnowego

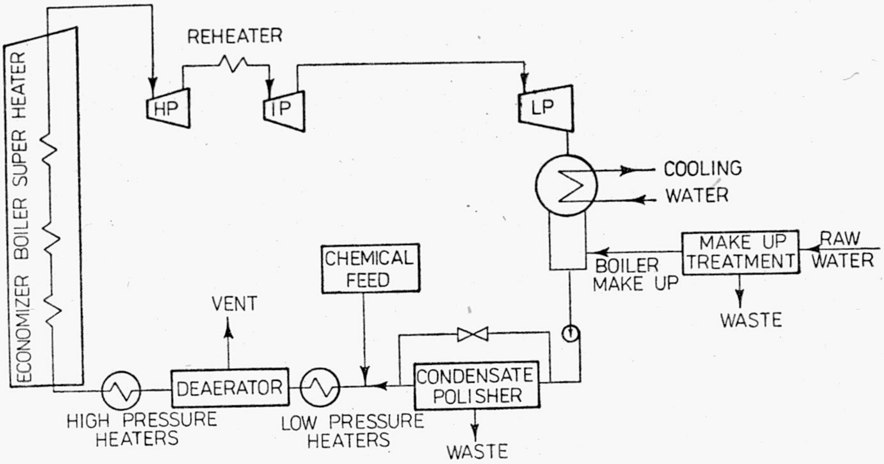

Fig. 3. Methods of controlling boiler water composition in once-through boilers

Rys. 3. Metody kontrolowania składu wody w kotłach przepływowych

2. PROBLEMS

The major problems which plagued the utilities in obtaining the desired quality of water at reasonable costs were the following.

2.1. FOULING OF ION-EXCHANGERS [2]

The ion-exchangers, especially the strong base exchangers, fouled readily if the make-up water contained organics, usually found in surface waters. Also, as cation exchangers deteriorated, it also sloughed organics which fouled the strong base anion exchangers. The fouling of the anion exchangers resulted in the following:

a) premature breakthrough,
b) poor quality effluents,
c) longer rinse.

2. 2. SHORT RUNS WITH CONDENSATE POLISHING MIXED BEDS

Especially when ammonia feed was introduced to increase the pH so as to reduce corrosion, the quality of the effluent suffered as sodium ion leakage was detected. This resulted in the following:

a) more frequent regeneration of the mixed bed,
b) increased regenerant costs as well as operating costs,
c) increased regenerant wastes.

2. 3. PARTICULATE SLIPPAGE AND DEPOSITIONS

"Crud" containing metal oxide, if present in condensate, tends to deposit on the ion-exchangers, and some of it passing through the ion-exchanger beds resultes in excessive pressure drops, consequently shorter run cycles and premature tube failures.

3. SOLUTIONS – MAKE-UP WATER. TO FOULING DUE TO ORGANICS

3. 1. CHLORINATION AND COAGULATION FOLLOWED BY ADSORPTION

Many surface waters contain high molecular organic acids, e.g. humic and fulvic acids [2] which are slow in diffusing out during regeneration. A solution to the problem was in treating the raw surface water with super chlorination and clarification by coagulation, followed by filtration and adsorption by activated carbon. The activated carbon was needed to remove the products of chlorine oxidation and removal of excess chlorine which is detrimental to ion-exchanger. However, the process had to be accurately controlled and the yield of water was limited by specific flow through the clarifier.

The effluent from the clarifier then passed an ion-exchanger system consisting of the following: cation exchanger – H^+ state, degassifier, weak base anion exchanger – base form, strong base exchanger – OH^- state (optional), mixed bed.

But, it was found that the then available weak base resins still fouled and proved not to be stable.

3.2. DEVELOPMENT OF SPECIAL RESINS

Two types of resins were developed by ion-exchanger manufacturers: macroreticular, or macroporous or fixed pore resins, as they are often called [23, 29], and isoporous resins [22]. The former are ion-exchangers with large pored structures in which the matrix is highly crosslinked. The latter are ion-exchangers with uniform porosity. In each case, during regeneration of the resins, the large organic anions desorb readily into the regenerating solution phase because they readily diffuse out of the large pores of the resins.

The weak base macroreticular resins proved to be highly stable and protected to a great extent the mixed bed. This, however, did not solve other problems which will be discussed later.

3.3. LAYERED OR STRATIFIED BEDS [14]

As the weak base macroreticular or macorporous resins proved applicable to organic removal, their use in the ion exchange systems treating surface waters became obvious. In addition, these ion-exchangers can be regenerated economically, i.e. stoichiometric regeneration. Since these exchangers cannot remove silica or carbon dioxide, strong base anion exchangers were also required. In view of this, the concept of layered or stratified beds emerged wherein weak base resin is placed over the strong base resin in the same vessel. The ratio of the weak base to strong base resin is determined on the basis of the ratio of the strong acids to weak acids present in the water.

During the operation of the layered beds, it is essential to backwash the bed after regeneration prior to the final rinse so that the weak base resin will be on top so as to contact the organic foulants first. However, while there is a reduction in fouling, some defouling maintenance should be practised. This consists of treating the layered beds with a brine-caustic soda rinse on a predetermined schedule.

3.4. MEMBRANE PROCESSES

Tests are now going on in several plants for utilizing membrane processes for treating make-up water with the view of eliminating fouling causing constituents as these remain in the reject stream. Reverse osmosis plays a dual role; it desalinizes the average water with permeate containing only 2 to 5% of the original salts and also being free of large ions and colloidal constituents. This process is essential in order not to foul the reverse osmosis membranes and unit.

To prevent calcium and magnesium precipitation, the feed can be softened with a cation exchanger which is regenerated with the reject stream from the reverse osmosis unit which contains only sodium salts.

In some plants ultrafiltration units, where membranes with specific pore sizes are utilized for rejecting fouling constituents, are checked as pretreatment for ion-exchange systems or reverse osmosis units [10].

In time, membrane processes will assume a greater role in desalination and prevention of fouling, although membranes themselves are subject to fouling. However, membranes processes need no chemical regeneration, but the wastes of which can become a disposal problem.

4. SOLUTIONS – CONDENSATE POLISHING. TO SHORT RUNS OF CONDENSATE POLISHING MIXED BEDS DUE TO LEAKAGE OR POOR QUALITY

4.1. USE OF HIGHLY CROSSLINKED ION-EXCHANGERS IN MIXED BEDS

It has been shown that poor performance of mixed beds can be due to:

(i) poor separation of cation exchanger from the anion exchanger or

(ii) the sloughage from the cation exchanger being entities with sulphonic groups is readily picked up by the anion exchanger, due to the sulphonic groups.

For all these problems, several solutions appeared. CALMON and SIMONS [8] showed that by using cation exchangers of 10% crosslinkage (Molar base) rather than that 8.5% crosslinkage they obtained excellent results in quality of effluents, high capacities, normalities and lower rinse requirement; the reasons given were the following: better separation of the exchangers due to the greater difference in densities between the cation and anion exchanger.

This technique is used by many plants. In others, macroporous resins which are higher crosslinked and have fixed pores are used successfully.

4.2. AMMONEX PROCESS

The use of copper tubes has been eliminated due to copper deposition in turbines. These have been replaced with steel tubes, which show less corrosion with increased pH, due to the addition of ammonia or hydrazine. With the condensate polishing systems, shorter runs were observed due to sodium release as the selectivity of cation exchanger for ammonium ions is above sodium (2.55 to 1.98, respectively). Therefore, the cation exchanger in the ammonium form in place of the hydrogen was introduced for the condensate polishing mixed beds [1, 20].

In the "Ammonex Process" of Cochrane [5], the anion exchanger after being regenerated with NaOH is further regenerated with ammonia solution, resulting in converting the trace quantity of cation exchanger, mixed in with anion exchanger, from the sodium to ammonium form, thus eliminating the sodium leakage. Longer service cycles and better effluents have been reported.

4.3. CALEX PROCESS

It has been pointed out above that by replacing the sodium with ammonium ions in the cation exchanger entrapped in the anion exchange resin on separation of the mixed bed results in better quality and in longer runs. Another method developed for getting the same results is the Calex process [9] in which the anion exchanger after being regenerated with NaOH is regenerated with $Ca(OH)_2$. The calcium replaces the sodium. The selectivity of the exchanger for calcium is much higher than for ammonium ions (5.6 to 2.55, respectively) so the ammonium ions in the condensate do not replace the calcium. Long runs and excellent quality of effluents are obtained [25, 31].

As the calcium hydroxide has a limited solubility and to prevent insoluble lime to get into the anion exchanger, a weak calcium salt solution is passed through a strong base anion exchanger in the OH form. This converts the salts to the OH so that a pure ionic solution is obtained for the conversion of the trace sodium cation exchanger to the calcium form [11].

4.4. SEPREX PROCESS [27]

Since separation of the mixed bed into its components is a major problem the Seprex Process was dereloped to get more complete separation. This was achieved by treating the separated anion exchange resin exchanger containing traces of fine cation exchanger with a 10 to 16% NaOH solution acting as the regenerant of the anion exchanger.

Since the cation exchanger in the Na-form has a higher density than the anion exchanger in the OH-form, it remains in the bottom of the vessels ready for acid regeneration. Similarly, the transferred anion exchanger is rinsed and sent to the tank holding the regenerated anion exchanger.

5. TO PARTICULATE DEPOSITION

5.1. USE OF FILTERS

Early condensate treatment systems had cellulose filters to remove "Crud" due to corrosion and erosion products [30]. However, later work [28] showed that these filters were not necessary during most of the runs. Only during start up the filters could have a function of preventing iron oxide deposition on the ion-exchangers of the mixed bed. Wirth [33] showed that iron could grow in the anion exchanger, resulting frequently in the rupture of the exchanger beads so as to require replacement of the resin due to the development of back pressure because of the fine beads and in addition, due to reduction in capacity. Today, few plants instal cellulosic filters and, if available, are commonly used only during start up of the boiler after shutdown.

5.2. LAYER OF HYDROGEN EXCHANGER ON TOP OF MIXED BED [3]

Part of the separated cation exchanger after regeneration with acid is kept separately and is placed over the freshly regenerated mixed bed so that the metallic oxides are neutralized and exchanged with the cation resin in the hydrogen form. After the run, the contaminated layer of cation exchanger is mixed with the cation exchanger of the mix bed on separation from the anion exchanger and the total of the cation exchanger is regenerated with acid, rinsed and once more part of it is placed on top of the mixed bed before beginning the service run.

5.3. POWDEX PROCESS [13]

When extremely fine (powdered) cation and anion exchangers are regenerated to their respective H^+ and OH^--forms and then mixed, they clump and form an excellent medium for filtration. This clumped mixture is used as a precoat on the outside of a porous cartridge element located in a pressure vessel. This mixture is capable of removing both ionic impurities as well as particulates. But, the major problem with this process is the fact that the resins cannot be separated to be regenerated and reused. This process is quite frequently used in the nuclear power plants where removal of particulate is of utmost importance.

With the advent of the use of ammonia for raising the pH, the cation exchanger in the Powdex Process is in ammonium form. The process can be used provided the condensate is low in electrolytes. Where the cooling water is brackish or seawater, preference is for the deep beds of ion-exchangers because of the fear of leaks.

5.4. ULTRASONIC CLEANING OF ION-EXCHANGE RESINS

It is difficult to remove metallic oxides once deposited on ion-exchangers, especially anion exchangers. As more plants have eliminated prefiltration of condensates prior to mixed beds, some suspended solids in minute quantities accumulate in the beds. Although conventional backwashing is carried out to remove particulate matter, its effectiveness has been limited.

HOLLOWAY and HOLLIFIELD [15] have patented the use of an ultrasonic method for cleaning deep bed ion-exchangers as a maintenance procedure. It is claimed that this cleaning procedure reduces the volume of chemical regenerant waste due to reduction in the regeneration dosages. This is of great importance, especially in nuclear power plants where reduction in waste volume is very important.

5.5. ULTRAFILTRATION

Some plants are applying ultrafiltration units, in which membranes with specific pore sizes are used, for the rejection of fouling constituents. These units are employed as pretreatment to ion-exchange or reverse osmosis.

6. FUTURE TREATMENT PROCESSES

6.1. TEMPERATURE STABILITY

The instability of strong base anion exchange resins at above 60° C when in the OH^- form does not permit their use close to the boiler and also the condensate has to be reduced to that temperature before passage through the mixed beds.

The work going on at various laboratories on organo-metallic materials indicate that new ion-exchangers may be developed which will prove to be stable at higher temperatures [16].

6.2. REMOVAL OF COLLOIDAL SILICA

Removal of colloidal silica either present in the water and/or formed in the strong-base resin during the adsorption stage is still a challenge.

Recent developments in strong base anion exchangers indicate that resins can be developed to remove colloide. The results are encouraging [24]. Membrane technology in reverse osmosis and ultrafiltration has made significant progress in reducing solids. Further progress may solve the problems.

6.3. REGENERANT WASTES

Disposal of regenerant wastes presents another challenge, especially in areas of limit ed water supplies. At present time, the regenerant wastes are diverted to available streams or injected in soil. Both methods add impurities or salts to already poor water supplies.

The Sirotherm Process [4] in which water is the regenerant is an effort in the direction of limiting the use of chemical regenerant.

A method for neutralizing the wastes from both the H^+ and OH^- cycles as well as from backwashings has been developed through the use of a carboxylic resin which has a high affinity for the H^+ ion and can be readily neutralized by the OH^- ion [12].

6.4. FOULING OF MEMBRANES

Preventive measures known to date to eliminate fouling of membranes are expensive both in terms of capital investment and operating costs.

The magnetic filters [26], more stable membranes, dynamic hyperfiltration [17], better engineering design of units and insolubilized enzymes [6] for specific destruction of organics may be further means for coping with the fouling problem.

6.5. BLOWDOWN OF COOLING TOWERS AND BOILERS

The blowdown of the above represents an environmental problem due to the large volume containing various salts.

Electrolysis offers means of reducing the reject volumes through concentrating the salts so that it can be readily disposed in appropriate areas. JORDAN et al. [19] describe a plant where the volume of blowdown was reduced from 3000 to 200 gpm and, therefore the evaporation pond could be reduced from 2000 to 150 acres. If softening were practised, further improvements could be obtained.

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OBECNE KIERUNKI UZDATNIANIA KONDENSATU

Artykuł stanowi przegląd metod otrzymywania ultraczystej wody zasilającej kotły wysokoprężne w elektrowniach. Dotyczy on głównie kondensatu i wody uzupełniającej.

Prezentowane podejście do zagadnienia polega na przedstawieniu, poprzedzonym wprowadzeniem, trzech głównych problemów dotyczących produkcji wody ultraczystej, a mianowicie zanieczyszczenia wymieniaczy jonowych, krótkich cykli pracy złóż mieszanych i zanieczyszczeń nierozpuszczalnych. Podano kilka sposobów rozwiązania każdego z nich. Przykładem może być wydłużenie cyklu pracy złóż mieszanych przez zastosowanie wysokousieciowanych żywic jonowymiennych lub procesów typu Ammonex, Calex i Seprex.

Omówiono również pozostałe problemy, takie jak: trwałość anionitów, krzemionka koloidalna i ścieki poregeneracyjne oraz zanieczyszczenia membran i odmulanie ścieków.

Trzydzieści dwie pozycje literatury umożliwiają sięgnięcie w razie potrzeby do źródeł oryginalnych.

GEGENWARTSPROBLEME DER KONDENSATAUFBEREITUNG

Der Bericht gibt eine Übersicht der Methoden zur Gewinnung von ultrareinem Wasser, das zur Speisung von Höchstdruckkesseln in Elektrizitätswerken dient. Das gilt besonders dem Kondensat und dem Ergänzungswasser.

Im Einführungsteil des Berichtes werden drei Hauptprobleme der Gewinnung von ultrareinem Wasser diskutiert. Dies sind: die Verunreinigungen der Ionenaustauschharze, die kurzen Arbeitsperioden von

Mischbettauschern und ungelöste Formen der Verschmutzungen. Der Verfasser stellt mehrere Lösungen eines jeden Problems dar. Als Beispiele werden die Verlängerung des Arbeitsganges von Mischbettauschern durch Anwendung von hochvernetzten Ionenaustauschharzen oder Verfahrensarten wie das Ammonex-, Calex- und Seprexverfahren angeführt.

Besprochen werden auch andere Fragen, wie z.B. die Haltbarkeit der Anionite, kolloides Silizium, die Regeneratlösungen, die Verunreinigungen der Membranen und das Abschlämmen.

32 Literaturhinweise ermöglichen dem Leser eine eventuelle Vertiefung und Klärung der o.e. Fragen.

СОВРЕМЕННЫЕ НАПРАВЛЕНИЯ В ПОДГОТОВКЕ КОНДЕНСАТА

Статья представляет собой обзор методов получения ультрачистой воды, питающей котлы высокого давления на электростанциях. Это касается главным образом конденсата и дополняющей воды.

Описанный подход к вопросу заключается в представлении, предшествующем введению, трёх главных проблем, касающихся производства ультрачистой воды, а именно загрязнение ионообменников, коротких циклов работы смешанных слоёв и нерастворимых загрязнений. Приведено несколько способов решения цикла работы смешанных слоёв путёв путём применения высокоструктурных ионообменных смол или процессов типа Аммонекс, Калекс и Сепрекс.

Обсуждены также остальные проблемы, такие как: устойчивость анионитов, силикагель и послерегенерационные сточные воды, а также загрязнение мембран и обесшламливание сточных вод.

Приведённые тридцать два названия в литературе дают возможность ссылаться, в случае надобности, на текстовой оригинал.