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# Some Aspects of Water Chemistry in Light Water Reactor Power Stations

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*Experience gained with nuclear power stations in service has led to new feedwater system arrangements, especially in the case of boiling water reactors. The consequences of forward pumping of h.p. condensate into the feedwater circuit and using a feedwater heater with deaerator in this type of plant are discussed. Mixed beds and precoat filters for condensate polishing are described in conjunction with present-day thermal cycles. The contribution closes with a brief survey of the layout and application of treatment plant for make-up water.*

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Large nuclear power stations with light water reactors require enormous amounts of cooling water. As it is no longer admissible to impose further thermal loading on rivers it has become necessary to use wet-type cooling towers or cooling by means of sea or brackish water. The consequent rise in salt content of the cooling water increases the risk of corrosion in the condenser resulting in a greater danger of cooling water leaking into the system.

Figure 1 shows a simplified circuit diagram for a BWR plant such as used in the Mühleberg (Switzerland) or Oskarshamn (Sweden) power stations. The BWR circuit shown in Fig. 2 corresponds to present-day projects. These diagrams form the basis for the following discussion of certain aspects of water chemistry in nuclear power stations with light water reactors.

## The Effect on the Water of Pumping Forward the Condensates from HP Heaters

### Introduction

The unit output of today's nuclear power stations with light water reactors has reached the same order of magnitude as conventional thermal power stations; it is restricted only by the size of the power supply system and its interconnections.

Experience gained with medium output nuclear power stations has enabled us to compare the various technical alternatives and arrive at optimum arrangements. Further knowledge has also been gained in the fields of water treatment and corrosion. New problems were encountered in comparison with the conditions pertaining in conventional plant. These problems included the very high degree of purity of feedwater required for nuclear steam generators, the high radiolysis oxygen content of the steam in BWR's and the behaviour of materials used in the steam generators of PWR's. The development of nuclear power stations led to

- universal use of reheating
- nickel alloy tubes instead of stainless steel in PWR steam generators
- stainless steel instead of copper alloys in BWR feedheaters
- forward pumping of h.p. condensate into the feedwater downstream of condensate polishing plant of BWR systems
- the use by certain manufacturers of a feedwater tank with deaerator in BWR plants.

In the early BWR plants the condensate from all heaters and water separators was fed into the condenser (Fig. 1). In the last few years, however, most BWR manufacturers have dropped this "cascade" system in favour of pumping the condensate forward (Fig. 2) and the circuit thus corresponds to a PWR or conventional system. Two reasons led to this arrangement; improved thermal efficiency and lower initial costs. Pumping forward the condensate from the feedheaters, reheater and, particularly, from the water separator, has definite advantages as far as polishing the feedwater is concerned.

One fundamental difference between a conventional and a saturated steam turbine is the behaviour of the impurities in the steam. In the case of a saturated steam turbine the solid and gaseous impurities, which have a high distribution coefficient between water and steam, are removed by condensation of 12 to 16% of the steam volume in the h.p. section. Water droplets carried over from the steam generator/water separator are the nuclei for condensation. The volatile impurities are primarily silica with possibly traces of organic or inorganic acids created by thermal decomposition of organic substances in the steam generator.

In contrast to the conditions pertaining in a saturated steam turbine the impurities in a conventional turbine are deposited on the blades, thus reducing its efficiency. The location at which they are deposited depends largely on the solubility of the impurities in the steam. Substances which are poorly soluble in steam or those which are carried over with water droplets are deposited on the first rows of blades whereas silica, which is fairly soluble

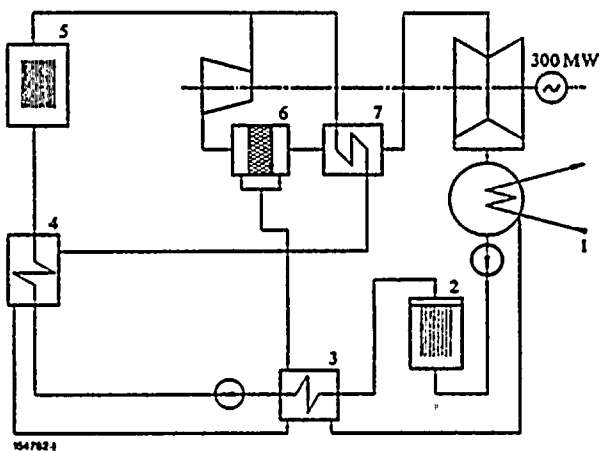


Fig. 1 - Diagram of 300 MW nuclear power station system

Mineral content of cooling water 250 ppm  
Condensate treatment by precoat filters

- 1 = Cooling water
- 2 = Condensate treatment plant
- 3 = LP feedheater
- 4 = HP feedheater
- 5 = Reactor with steam generator
- 6 = Water separator
- 7 = Reheater

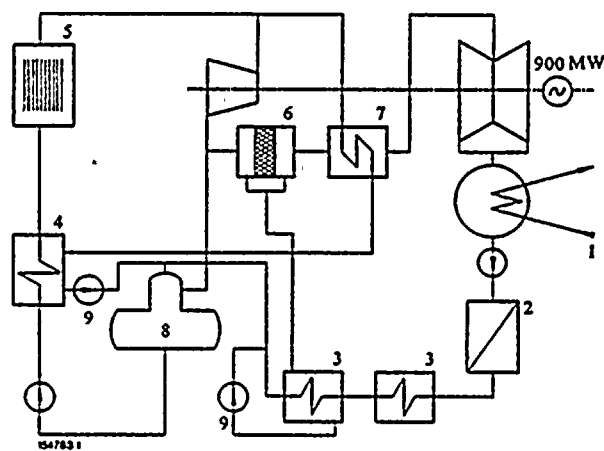


Fig. 2 - Diagram of 900 MW nuclear power station system

Mineral content of cooling water 1000 ppm  
Condensate treatment by mixed bed filters

- 1 to 7 as Fig. 1
- 8 = Mixer heater with deaerator
- 9 = Condensate pumps

in steam, is deposited on the final dry stages. Traces of volatile acids ( $\text{HCl}$ ,  $\text{CH}_3\text{COOH}$ ) in the steam are precipitated quantitatively from the steam during the first condensing process and form a relatively concentrated acid solution which, experience has shown, can lead to local corrosion damage.

In general it has been found that there is less tendency for the impurities in a saturated steam turbine to collect or lead to corrosion than in a conventional turbine. Consequently it would be permissible to allow a greater proportion of impurities, such as silica, in the steam of a saturated steam turbine than in a conventional one.

Examining the condensate from the water separator of a BWR turbine shows the water to contain very little impurities. On the one hand the water of a BWR is very clean, and on the other, the amount of reactor water carried over is very small ( $< 0.1\%$ ). However, the impurities comprise partly activated corrosion products and possibly uranium fission products, and may therefore be highly radioactive.

It is obvious that it would not be very satisfactory to cascade this condensate to the condenser and thus contaminate the resins in the condensate polishing plant. If the condensate polishing plant uses precoat filters the spent resins would have to be stored as radioactive waste. If it uses mixed bed filters it would be very costly to decon-

taminate the spent regeneration solutions. It is therefore of advantage to return this condensate direct to the reactor. In this case the impurities are absorbed by the clean-up demineralizer, whose function is to treat radioactive water. Treating the condensate from the water separator means that the clean-up demineralizer has to deal with only 2 to 3% more impurities.

Cleaning the steam by means of expansion in the h.p. turbine is fully effective only if the liquid phase, enriched with impurities, is kept entirely separate from the steam. Unfortunately, as far as we know, there is no accurate method of determining the efficiency of the turbine water separator. The methods involving radioactive tracers such as  $^{24}\text{Na}$  cannot be applied in this case.

Further cleaning is carried out in the reheater where any water droplets carried over from the water separator are vaporized and some of the minerals they contain are deposited. The end product is the l.p. steam which is cleaner by several orders of magnitude than the h.p. steam and contains virtually no long-lived solid radioisotopes. Only gaseous radioisotopes (e.g. inert gases and nitrogen) can enter the condenser. Nevertheless, small quantities of radioactive matter can enter the condenser in the liquid phase if water samples are returned to the condenser, during flushing and similar operations. The high-pressure condensate formed during

turbine start-up is also cascaded direct into the condenser. In fact, reactor water can be blown down into the condenser during emergency shutdown. Viewed as a whole, however, the sum of all these impurities represents only a small fraction of those normally removed from the steam in the water separator during the life of a nuclear power station.

This means of steam cleaning applies to BWR plants of the future but the principle can be seen in any PWR system. These plants, where the condensate is pumped forwards, correspond to the diagram shown in Fig. 2. If phosphates are used for treating the steam generator water it then becomes possible to determine the carry-over in the condensate from the water separator or the feedwater but not from the condenser. The carry-over measurements can be carried out more accurately by using  $^{24}\text{Na}$  instead of phosphates or Na.

### Using a Deaerator in a BWR Cycle

The two main reasons for using a deaerator are to replace the traditional surface preheater, comprising a bundle of costly stainless steel tubes, by the less expensive mixing heater and also to provide a feedwater tank between the condensate pumps and the feedwater pumps.

In a conventional or PWR cycle a mixing heater deaerates the feedwater. In a BWR system the steam

used in the deaerator for heating purposes contains 20 to 30 ppm radiolysis oxygen and can increase the content of the dissolved oxygen in the feedwater. Excessive concentrations of oxygen in the feedwater are avoided by providing adequate venting for non-condensable gases in the condenser. BWR manufacturers require that there be no more dissolved oxygen in the feedwater than at equilibrium in the reactor water. However, it has been known for some time that carbon or low-alloy steels corrode less in water with a low oxygen content than in water which is absolutely free of oxygen [1 to 3]. Certain power station operators have shown [4, 5] that by using neutral water the quantity of corrosion products carried into the boiler can be reduced by conditioning the condensate and feedwater with small quantities of hydrogen peroxide. Consequently, as the mixing heater supplies feedwater with a small amount of dissolved oxygen, it has a favourable effect on the amount of corrosion products because it effectively decreases the formation of soluble ferrous hydroxide  $\text{Fe}(\text{OH})_2$ . On the other hand, the BWR manufacturers stipulate that the oxygen concentration in the feedwater due to radiolysis in the reactor water does not exceed a prescribed limit (about 0.2 ppm). It thus becomes essential to vent-off the non-condensable gases in the condenser. Similarly, it is also essential to provide optimum deaeration of the condensate in BWR systems because free oxygen attacks the brass condenser tubes and any ingress of air into the condenser would introduce nitrogen which forms nitric

### Comparison of mixed bed and precoat filters

	Mixed bed filters	Precoat filters
Advantages	High exchange capacity permits operation with relatively large leak-in of cooling water	Excellent filtration of colloids and suspended substances
	Very low cost per $\text{m}^3$ for demineralization of cooling water leaking in	Only solid radioactive waste which can be stored without further treatment
Drawbacks	Moderate filtration of suspended substances and colloids, leakage of these from filter during load transients	Small exchange capacity permits operation with only small amounts of cooling water leaking in
	Liquid radioactive wastes which are expensive to decontaminate and store (as the regenerative agents are concentrated solutions they cannot be decontaminated by ion exchange)	Reactor or turbine shut-down often leads to renewal of precoat
		High operating costs
		Very high cost per $\text{m}^3$ for demineralization of cooling water leaking in

acid, in the reactor. The feedwater can therefore be conditioned only by adding oxygen or hydrogen peroxide after it has passed through the condensate treatment plant. Air is not suitable because of its nitrogen content.

### Condensate Polishing Plant

This is an indispensable component of BWR and PWR systems with once-through steam generators. There is a trend at present to equip PWR systems that have natural circulation steam generators also with condensate polishing plants (cpp's) to ensure extra clean feedwater under all conditions.

Two cpp systems are used in BWR plants: mixed bed filters and precoat filters. The latter use finely pulverized ion exchange resins. Both types have been described in detail in the literature [6, 7, 8, 9] and need not be dealt with here. However, an attempt is made in the Table to define the various criteria for selecting either type.

The main criterion is the quantity of salts entering the system during operation of the power station. This quantity depends on the known salinity of the cooling water and also on the amount of leakage at the condenser which is very difficult to predict as this depends, amongst other factors, on the salinity of the water.

If the cooling water has a low salinity (e.g. circulating water from a dry-type cooling tower or river water with less than 250 ppm) then precoat filters are ideal. They efficiently filter insoluble and colloidal impurities from the condensate although their demineralizing capacity is relatively small. Some of the more interesting experience gained at the Mühleberg nuclear power station is summarized in the following.

At the start of commissioning it was found that the exchange capacity of a resin charge was exhausted after one or two days. After two to three months operation it had reached a life of about a fortnight. The criterion now for replacing a charge is excessive pressure loss and no longer exhaustion of the exchange capacity. The excellent performance of the precoat filters is primarily a result of the purity of the condensate entering the filters. Under steady-state conditions at 25 °C it was found to contain 0.01 to 0.02 ppm suspended matter with a conductivity of 0.09 to 0.12 µmho/cm. The amount of cooling water leaking in is 5 to 10 l/h with a salt content of 250 ppm. These values were estimated from measurements with <sup>36</sup>Cl in the reactor water and correspond to a 5% drop in anion capacity over a two-week period.

In practice, however, the resin consumption is somewhat higher than can be determined from the chemical composition of the condensate. During commissioning, flow-

back due to shut-down of condensate or feedwater pumps can cause faults at the filters, necessitating replacement of the resin. Cartridge-type filters are somewhat more susceptible than the horizontal plate ones in losing the precoat. The circulating pumps for the filtering plant have only a small capacity and cannot prevent backwash occurring during an abnormally fast flow-back of water.

The main drawback of precoat filters is their small deionizing capacity. The total capacity of the pulverized pure resins used is in the order of 4 eq./kg dry substance. The useful capacity is considerably smaller, particularly when used with a BWR plant. This can be explained by the following example:

#### Data of nuclear power station with BWR:

Rating	900 MW
Max. permissible conductivity of reactor water	1.00 µmho/cm at 25°C
Steam output	5500 t/h
Clean-up capacity	80 t/h max (example)
Evaporation ratio of reactor water	1:69
Conductivity of the treated water	0.06 µmho/cm at 25°C

From these values we can calculate the maximum conductivity of the feedwater which agrees with the maximum conductivity of the reactor water of 1.00 µmho/cm.

#### Conductivity of impurities in reactor water:

$$1.00 \text{ to } 0.06 = 0.94 \text{ µmho/cm}$$

#### Maximum conductivity of feedwater:

$$0.06 + \frac{0.94}{69} = 0.06 + 0.014 = 0.074 \text{ µmho/cm at } 25^\circ\text{C}$$

The useful capacity of the pulverized resins is naturally dependent on the permissible ionic leakage. Balthazar [7] refers to a useful capacity of the order of 2 eq./kg with ion leakage of 0.1 µmho/cm in a plate-type filter plant with progressive precoat. In our opinion a maximum of 1 eq./kg can be used in the calculation for the required 0.074 µmho/cm. Under these conditions an ingress of 1 m<sup>3</sup> of cooling water with a mineral content of 20 meq./l (wet cooling tower operation) corresponds to a consumption of about 20 kg of anion and 40 kg of cation exchanger resins. For the same conditions a mixed bed filter would require merely a few kilogrammes of reagents.

However, the main drawback of mixed bed filters compared to precoat filters is the contamination of the spent regeneration chemicals by radionuclides. Nevertheless there are two important factors to be considered:

- The increase in contamination by radionuclides is constant. In BWR plants with a clean cycle and a condenser with no leakage the mixed bed filter would require regeneration only once or twice per year. Periodic back washing removes only solid impurities and decreases the pressure drop. Should cooling water leaking in lead to more frequent regeneration, the radioactive contamination of the reagents would be much less than is the case with routine regeneration.

- In first generation BWR systems all condensate, including that from the water separator, containing most of the radionuclides, passed through the mixed bed filters. The proportion of radionuclides to be removed was very high. Where the condensate is pumped forward, the mixed bed filters are contaminated merely by the decay products of certain noble gases (Kr, Xe) but as their retention time in the condenser is very short the amount of contamination is negligible.

Another drawback of mixed bed filters as opposed to precoat filters is their poorer performance in filtering colloids and insoluble substances. However, the degree of feedwater purity demanded by reactor manufacturers can be achieved with the mixed bed filter. The contamination tolerated so far has not had a detrimental effect on the fuel. The purity of the feedwater has been raised considerably by measures implemented independently of the cpp. Non-ferrous metals in the feedwater-heater were replaced by stainless steel and attempts are being made to reduce the amount of dissolved iron by slightly increasing the concentration of dissolved oxygen. A considerable reduction of the oxidation products in the raw condensate preceding the cpp was brought about by very careful supervision of the cleanliness of all components during assembly and installation, and by flushing the system before commissioning and before each start-up. These precautions may be regarded as excessive by many but, by rigidly adhering to this policy at Mühleberg it was found that after a few weeks of operation the raw condensate upstream of the cpp was of the required high degree of purity required of the feedwater at reactor inlet.

Because of the high ion exchange capacity of the mixed bed filter a turboset can continue operation even if there are cooling water leaks and repairs to the condenser can be postponed to a convenient time. It should be pointed out once again that in a BWR plant the condenser cannot be repaired during service as in a conventional

plant. The high radioactivity level (particularly of  $^{16}\text{N}$ , half-life = 7 s) precludes access to the water boxes with the machine in operation.

Considering the above criteria it can be seen that the mixed bed filter is an attractive proposition where the cooling water has a high salt content, i.e. sea water or river water concentrated in a wet cooling tower. The advantages of the precoat filter can be exploited where the aggressivity and salt content of the cooling water are low enough to make water leakage in the condenser an acceptable risk. It is not possible at present to set a salt content level, above which mixed bed filters must be used. The risk must be estimated in each individual case by the manufacturers and client. As the corrosion process is relatively slow it will not be possible to quote concrete figures for some years to come.

The field of application of precoat filters could be extended by fitting the condenser with tubes of corrosion-resistant material, such as titanium, but considering the large surface area required for a light water reactor power station, the cost would be prohibitive for the foreseeable future.

## Make-Up Water Treatment Plant

The difference between the treatment plant for make-up water of a PWR and BWR system is not always immediately apparent from the specifications. PWR systems have a higher water consumption because of the continuous blow-down of the steam generator. In BWR systems virtually all water which has once been introduced into the system is reclaimed and reused. Accordingly there are different arrangements for the two types of power station.

Demineralization plants perform the following tasks:

- pre-treatment (flocculation, filtration)
- main demineralization (cation exchange,  $\text{CO}_2$  removal, anion exchange)
- polishing (removing the last traces of minerals in a mixed bed filter).

The arrangement of the main demineralization plant depends on the type of power station; counter-flow systems are to advantage for PWR plants. The high initial outlay is justified by the savings in chemicals during service. BWR plants are equipped with the simple and inexpensive traditional systems. The cost of water does not justify large outlay to save on chemicals.

Fully automatic plants are recommended for pre-treatment and main demineralization; only the mixed bed

filters require manual regeneration. This means, however, that the mixed bed filters need be used only as polishers so that they require regeneration only about twice a year, as is the case with some PWR power stations in operation at present. In order to avoid overloading the mixed bed filter operation of the main demineralizer is interrupted as soon as the conductivity starts to rise. Silica leakages, which cannot be determined by conductivity measurements, are prevented by making the cation exchanger capacity somewhat smaller than that of the anion exchanger. The end of a working cycle is indicated by a sodium leakage. This technique can be applied only where the composition of the raw water remains constant. If this is not the case an automatic analyser must be installed for measuring the silica in the make-up water and interrupting the working cycle as soon as there is a  $\text{SiO}_2$  leakage.

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