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(54) Titre : PROCÉDE DE NETTOYAGE DU DISPOSITIF PRODUCTEUR DE VAPEUR D'UN REACTEUR A EAU SOUS
PRESSION

(54) Title: METHOD OF CLEANING THE STEAM GENERATOR OF A PRESSURIZED WATER REACTOR

(57) **Abrégé/Abstract:**

The invention relates to a method for cleaning steam generating devices of a compressed water reactor, whereby said devices are treated on the secondary side, at high pressure and high temperature, with an aqueous cleaning solution which contains EDTA, a reducing agent and an alkalisng agent. According to the invention, morpholine is used as an alkalisng agent. A molar morpholine-concentration, which is at least the same size as the molar concentration of EDTA, is thus selected.

Abstract

The invention relates to a method for cleaning steam generating devices of a compressed water reactor, whereby said devices are treated on the secondary side, at high pressure and high temperature, with an aqueous cleaning solution which contains EDTA, a reducing agent and an alkalising agent. According to the invention, morpholine is used as an alkalisation agent. A molar morpholine-concentration, which is at least the same size as the molar concentration of EDTA, is thus selected.

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Method of cleaning the steam generator of a pressurized water reactor

The invention relates to a method of cleaning the steam generator of a pressurized water reactor. A steam generator of a pressurized water reactor usually comprises a vessel in whose lower region a large number of, for example, U-shaped heat exchanger tubes through which primary coolants flow are arranged. In the upper region of the vessel, there are further internal fittings such as steam separators and steam dryers. While the heat exchanger tubes comprise corrosion-resistant alloys, the vessel, auxiliary structures serving to fix the heat exchanger tubes and parts of the secondary circuit through which secondary coolants flow are partly made of materials having a lower corrosion resistance, for example carbon steel. The parts mentioned are therefore subject to corrosion at the operating temperatures which prevail. During operation, corrosion products, mainly magnetite, are formed in the secondary circuit and go into the steam generator where they deposit on the bottom of the vessel and in spacers between tubes and grow as a coating on the surface of the heat exchanger tubes. To ensure the integrity and satisfactory performance of steam generators, in particular unhindered heat transfer, cleaning work is, if necessary, carried out during annual maintenance in order to remove the sludge formed by the deposits and the coating on the heat exchanger tubes by chemical means.

For this purpose, the steam generator is filled stepwise with cleaning liquid until the exchanger tubes are fully immersed. A customary cleaning solution known, for example, from US 4,632,705 comprises a complexing acid such as

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ethylenediaminetetraacetic acid (EDTA), a reducing agent, for example hydrazine, and ammonia as alkalizing agent. Alkaline conditions are necessary in order to keep dissolution of material from the parts of the secondary circuit which consists of carbon steel or low-alloy steels as low as possible. In addition, a corrosion inhibitor is added for this purpose. In the case of a method which is known from DE-A 198 57 342 and likewise employs hydrazine as reducing agent, morpholine (tetrahydro-1,4-oxazine) is used as alkalizing agent. Morpholine is significantly less volatile than ammonia, so that only a correspondingly smaller proportion goes into the vapor phase. In cleaning methods of the present type, the usual procedure is to carry out a sudden depressurization via valves of the fresh steam system located downstream of the steam generator at particular time intervals, leading to vigorous boiling and strong turbulence in the cleaning liquid. In this way, the cleaning solution is mixed so that the complexing agent can dissolve the magnetite after reduction. Since the proportion of morpholine in the vapor phase is significantly lower than that of ammonia, significantly less environmentally polluting alkalizing agent gets into the environment on depressurization than in the case of methods employing ammonia. In terms of the cleaning method, the small loss of alkalizing agent has the significant advantage that the pH remains virtually constant to the end of cleaning. This results in dissolution of metal of construction being reduced compared to methods employing ammonia in which, owing to the loss of ammonia, the pH drops to values close to neutral toward the end of the cleaning time.

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According to an aspect of the invention, there is provided method for cleaning steam generating devices of a compressed water reactor in which said devices are treated on a secondary side, at raised pressure and raised temperature, with an aqueous cleaning solution which contains EDTA, a reducing agent and morpholine as an alkalizing agent, wherein the use of a cleaning solution in which the morpholine concentration and the concentration of EDTA are present in a molar ratio of 1:1 to 6:1, and in which at least one of hydrazine and formaldehyde is used as reducing agent, whereby the ratio of at least one of hydrazine and formaldehyde to EDTA is 1:6 to 1:1.

10 It is an object of one aspect of the invention to provide a cleaning method for the steam generators of a pressurized water reactor, by means of which effective cleaning with further reduced dissolution of metal of construction is possible without

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addition of a corrosion inhibitor.

It has

surprisingly been found that use of a cleaning solution in which the molar morpholine concentration is at least as great as the molar concentration of EDTA makes it possible to achieve more gentle cleaning, viz. cleaning which is less aggressive toward of metal of construction, compared to ammonia methods.

The absolute concentrations of the specified constituents in the cleaning solution naturally depend on the amount of deposit to be removed in each case, so that these may be present in relatively high concentrations. The abovementioned gentler cleaning effect is nevertheless observed when morpholine is present in a molar concentration which is the same as or greater than that of EDTA.

The molar ratio of morpholine to EDTA is preferably in the range from 1:1 to 6:1. Optimal results are achieved when it is 4:1. The latter molar ratio corresponds to a mass ratio of 1.2. A particularly good cleaning action is achieved when the molar ratio of hydrazine to EDTA is in the range from 1:6 to 1:1. Preference is given to a molar ratio of 1:3, which corresponds to a mass ratio of 0.04. Apart from the particularly preferred hydrazine, it is also possible to use other reducing agents, in particular formaldehyde.

Example:

A cleaning solution suitable for cleaning a steam generator comprises 60 g/l of EDTA (= 0.205 mol/l), 71.5 g/l of morpholine (= 0.821 mol/l) and 2.2 g/l of hydrazine (= 0.068 mol/l). Such a solution has a pH of about 9. The molar ratio

of morpholine to EDTA is thus 4:1, and that of hydrazine to EDTA is 1:3.

A preferred variant of the method provides for cleaning to be carried out during running-down of the reactor. As soon as the temperature in the steam generator is about 160°C, the constituents of the solution are introduced in concentrated form in such an amount that the abovementioned concentrations are obtained after addition of water. The pressure in the steam generator is, depending on the cleaning temperature, from about 6 to 10 bar. The cleaning solution is brought to boiling by means of sudden depressurizations distributed over the entire cleaning time, so that unconsumed chemicals come into contact with the deposits. Below about 140°C, cleaning can no longer be carried out effectively.

To examine the effectiveness of cleaning solutions employing morpholine in comparison with ammonia when using the same method, the tests described below were carried out:

In a laboratory autoclave made of stainless steel, 11.5 g of magnetite sludge having an iron content of 72.5% by weight from the steam generator of a pressurized water plant were treated with about 1 l of the above-described cleaning solution at a temperature of 160°C for 8 hours, with sudden depressurizations being carried out a number of times in order to achieve intimate mixing. The water removed during the course of evaporation and the cleaning solution removed from the autoclave for sampling purposes were fed in again. Coupons of carbon steel were positioned below the surface of the liquid by means of a Teflon-coated suspending device located in the autoclave.

2 experiments were carried out under these boundary

conditions, with ammonia/EDTA being employed in one case and morpholine/EDTA being employed in the other case and the respective alkalizing agent being metered in so that a pH of 9 was established. As a result of the cleaning liquid taken off being fed back in again, this value remains virtually constant to the end of cleaning so that the above-described effect of increased attack on the metal of construction as a result of the reduction in pH was suppressed. At the end of the experiments, the amount of iron dissolved from the coupons and from the sludge was determined. In both cases, the ratio of dissolved sludge to initial amount of sludge was found to be 95%. Both cleaning solutions exhibited a comparable effect in respect of the dissolution of magnetite sludge. However, while the proportion of iron dissolved from the carbon steel coupon in the experiment using ammonia was 20%, this proportion was only 15% in the morpholine experiment. The corrosion action on the carbon steel was thus lower in the case of the cleaning solution containing morpholine. In the cleaning test using ammonia, an average of 27 μm of material was removed, which corresponds to an average dissolution rate of $34 \text{ g/l}^*\text{h}^*\text{m}^2$. In the morpholine experiment, an average removal of material of 21 μm or an average dissolution rate of $20 \text{ g/l}^*\text{h}^*\text{m}^2$ was observed. Since the pH was kept virtually constant in both cases, the poorer result of the ammonia experiment cannot be attributed to a reduction in the pH. Rather, an effect resulting from the combination EDTA/morpholine appears to be present.

Differential thermal analyses carried out by the applicant on ammonia/EDTA and morpholine/EDTA indicates a greater thermal stability of the system morpholine/EDTA when the specified molar ratios are adhered to. It is known that EDTA decomposes at relatively high temperatures, forming corrosive decomposition products, for example iminodiacetic acid. This

problem has hitherto been countered by a shortened cleaning time or by a reduced cleaning temperature. The disadvantages which result from this are obvious. On the other hand, wider time windows can be exploited in the method proposed. Furthermore, cleaning at temperatures above 180°C should also be possible because of the higher thermal stability of morpholine/EDTA.

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CLAIMS:

1. Method for cleaning steam generating devices of a compressed water reactor in which said devices are treated on a secondary side, at raised pressure and raised temperature, with an aqueous cleaning solution which contains EDTA, a
5 reducing agent and morpholine as an alkalizing agent,

wherein the use of a cleaning solution in which the morpholine concentration and the concentration of EDTA are present in a molar ratio of 1:1 to 6:1, and in which at least one of hydrazine and formaldehyde is used as reducing agent, whereby the ratio of at least one of hydrazine and formaldehyde to
10 EDTA is 1:6 to 1:1.
2. Method according to claim 1,

comprising a molar ratio of morpholine to EDTA of 4:1.
3. Method according to claim 1 or 2,

comprising a molar ratio of at least one of hydrazine and formaldehyde
15 to EDTA of 1:3.
4. Method according to any one of claims 1 to 3,

wherein a temperature of 140°C to 200°C is maintained during the cleaning.