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(54) **CHEMICAL CLEANING PROCEDURE FOR HEAT EXCHANGERS**

(57) Applicable to exchangers made up of a set of tubes from a primary circuit, these tubes being separated by separation plates, said tubes and said plates being coated in use with deposits adhering to them of materials from erosions, corrosions and impurities in the secondary circuit, these materials particularly being formed of metals and metal oxides such as magnetite and metals such as copper, this procedure comprising a first phase of elim-

inating the metal oxides and in the event of the cleaning being done on materials containing copper, a second phase for decoppering and eliminating any copper compounds, in which a water solution, containing the following reagents is inserted into the steam generator: Citric acid, 0.5-10% in mass Ascorbic acid 0.3-5% in mass The process is carried out at a temperature of 20°C-70°C And the pH for the process starts at values of from 1 to 4.5

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Description

[0001] This invention concerns a chemical cleaning procedure for heat exchangers performed in different phases, including in particular an acid phase for dissolving metal oxide deposits, and a later decoppering stage. The phases involved in the standard procedure are as follows:

- Initial filling and testing the system; guaranteeing the system is sealed with mounting at temperature.
- An acid phase: the stage for dissolving metal oxide deposits (mainly iron); in which a water solution of citric acid and ascorbic acid and/or formic acid, with a pH from 1-6a is injected in a closed continuous circuit
- Emptying and rinsing: eliminating solvent residues
- Decoppering phase, when the process is performed on alloys containing copper: this is a stage for dissolving any copper possibly redeposited during the acid phase, which uses ammonia, ammonium bicarbonate and hydrogen peroxide as reagents, keeping the pH at values over 8
- Final rinse

[0002] In this context the proposal is to perform a procedure for partially dissolving any metal oxide deposits (acid phase) followed by a decoppering stage, with a recirculation loop.

[0003] Although this is for general application, the procedure covered by this invention is particularly designed to be applicable to cleaning heat exchangers of steam generators at PWR-type nuclear power stations, although it could also be used in heat exchangers in other installations with the same problem.

[0004] The steam generator consists of a heat exchanger, as well as its housing vessel and auxiliary items, in which water is made to circulate at high pressure and temperature from the reactor, or from another heat source, through a set of tubes, transferring said heat to the water in the secondary circuit.

[0005] While the installation is being used its heat exchangers are significantly affected by dirt and blockages connected with the depositing of corrosion products from the secondary circuit, which mainly include magnetite and other iron oxides; there could also be copper deposits, amongst others.

[0006] These dirtying and blocking phenomena modify the thermo-hydraulic and vibratory performance of the heat exchangers, which can lead to problems with safety, performance and also of duration of the part in operating conditions.

[0007] Hence, since these deposits are undesirable, a cleaning operation has to be carried out on the heat exchanger of the steam generator, according to a specific application, normally during all the regular stoppages taking place at a nuclear power station for reloading fuel.

[0008] In order to significantly reduce the problems stemming from dirtying by deposits of unwanted particles on the level of the tubular plates and separators, in which particularly metal deposits are left behind, a preventive chemical cleaning of the steam generator is required so as to maintain this in a condition with optimum capacity for heat exchanging, without the corrosion of the cleaning process managing to cause any deterioration that could affect the safety of the operation.

State of the art

[0009] Different procedures for cleaning steam generators are known.

[0010] US 4632705 describes a process for eliminating deposits accumulated in the restricted areas of the steam generator of a nuclear power station, in which the concentration of a water-based organic cleaning agent is increased in restricted zones, in respect of the concentration existing in the other zones. The solution is heated with an initial pressure to prevent the solution from boiling and the pressure is then reduced to perform intermittent boiling. After some time has elapsed the cleaning agent is increased and removed with the dissolved deposits, and a phase for eliminating the copper at subatmospheric pressure is started, with the addition of an oxidising agent, in particular hydrogen peroxide. The operating temperatures vary depending on whether one is attempting to eliminate ferrous or copper residues, from about 120°C-130°C to 30°C-40°C. The usage of citric acid as one of the reagents is described. Nitrogen is used as an element for counter pressure in the steam generating chamber.

[0011] US 2010/0313913 A1 describes a physical-chemical method for cleaning the chamber of the secondary circuit of a heat exchanger in a nuclear installation, which includes drying the secondary circuit and inserting a cleaning solution into the chamber for treating the deposits.

[0012] EP 0 458 533 A1 describes a procedure for eliminating sludge and products of corrosion from a heat exchanging chamber, in which a chemical cleaning agent is introduced, and maintained for a period from 13 to 70 hours, the agent being based on iron containing chelate at a temperature of from -120°C to 100°C, with generation of pressure pulses.

[0013] US 5 764 717 discloses a procedure for eliminating scale, sludges, residues and other deposits from the inside of the vessel of a heat exchanger, such as a steam generator of a nuclear power station. It includes generating pressure pulses in a highly basic agent containing amines in a water solution. The solution is made to recirculate through a filter.

[0014] Each of these procedures involves its own particular difficulties. The working temperatures, which can be very high, entail an always undesirable energy consumption. The same thing occurs in the event of these being low.

[0015] Another great disadvantage is the duration of the processes, which generally last for several dozen hours; given that the idle time of the power station is a critical matter, all the operations must be performed in a short a time as possible. Since the steam generator is furthermore a unique and essential part of the circuit, it furthermore requires a prior complete shutdown of the power station, and the operations for maintenance of this component have to be performed at the same time as the other operations are carried out for reloading fuel and maintaining the relevant components of the main and auxiliary circuits.

[0016] It is desirable for the process for cleaning the steam generator to last only a short time with a minimum consumption of energy in this process, as achieved in this invention.

Description of the invention

[0017] The invention being proposed describes a procedure for preventive chemical cleaning which eliminates the deposits found in:

- The bundle of tubes of the exchanger
- The separating plates
- In the laminar water passages of the different separating plates
- The flow distribution plate
- The tubular plate
- The common items of the secondary circuit of the exchanger (casing, housing, etc.)

[0018] Hence, according to one embodiment of the invention, from 200 Kg of deposits can be eliminated from the steam generator of a standard 900 MW power station in a conventional reloading operation.

[0019] Furthermore, according to standard specifications, the maximum admissible values for free corrosion and galvanic corrosion are from 1 μm for stainless materials and nickel-based alloys to 100 μm in low-alloy materials, carbon steels or welded joints. The intention is thus to ensure that metal oxide deposits are dissolved with a minimum corrosive effect on the base material of the installation, as is achieved with the procedure described herein.

[0020] One objective is for the amount of gaseous effluents to be as low as possible. The lowest possible amount of ammonia must specifically be obtained.

[0021] The effluents produced also meet the conditions required to be acceptable for installations for processing and conditioning nuclear waste. These installations can be at the plant itself or external.

[0022] The procedure for the invention is thus one of chemical cleaning of heat exchangers which mainly comprises the following phases:

- An acid phase with the aim of partially dissolving the deposits of oxides located on the tubes as well as the ones that obstruct the passages inside the plates;
- A decoppering stage for the deposits found on the steam generator and for any copper which could have been redeposited as a result of the first stage.

[0023] The operations are carried out dynamically, with an initial filling and the injection of solvents in different stages over time, or by preparing the mixture and filling the exchanger chamber with this.

[0024] The later explanation refers to the following compounds:

- Citric acid:

- $\text{C}_6\text{H}_8\text{O}_7$: indicated as AH_3 (citric acid)
- $\text{C}_6\text{H}_7\text{O}_7^-$: indicated as AH_2^-
- $\text{C}_6\text{H}_6\text{O}_7^{2-}$: indicated as AH^{2-}
- $\text{C}_6\text{H}_5\text{O}_7^{3-}$: indicated as A^{3-}

- Ascorbic acid

- $\text{C}_6\text{H}_8\text{O}_6$: BH_2 (ascorbic acid)
- $\text{C}_6\text{H}_7\text{O}_6^-$: BH^-
- $\text{C}_6\text{H}_6\text{O}_6^{2-}$: B^{2-}

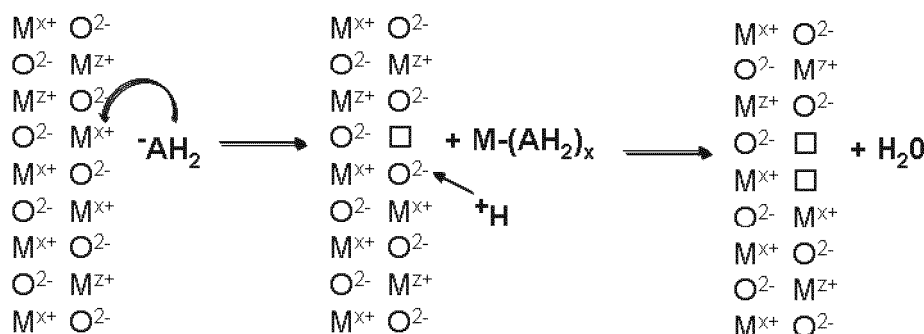
[0025] The following reagents are used in these phases, giving rise to the reactions indicated in the following table:

Reagents	Formula	Acid-basic and Redox reactions
Citric acid	$C_6H_8O_7$	$AH_2^- \rightarrow AH^{2-} + H^+ \text{ pKa}_1 = 3.15$ $AH_3 \rightarrow AH_2^- + H^+ \text{ pKa}_2 = 4.77$ $AH^{2-} \rightarrow A^{3-} + H^+ \text{ pKa}_3 = 6.40$
Ascorbic acid	$C_6H_8O_6$	$BH_2 \rightarrow BH + H^+ \text{ pKa}_1 = 4.1$ $BH \rightarrow B^{2-} + H^+ \text{ pKa}_2 = 11.4$ $C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e^- E^\circ = 0.39V$ $C_6H_6O_6$: Dehydroascorbic acid
Ammonia	NH_3	$NH_4^+ \rightarrow NH_3 + H^+ \text{ pKa} = 9.25$

[0026] There are two types of dissolving mechanisms:

1. Dissolution followed by a combination: the O^{2-} ions of the surface are attacked by H^+ ions to form HO^- (in a basic medium) or H_2O (in an acid medium) which destabilises the structure
2. Adsorption followed by dissolution: a strong combining binder (AH^{2-}) is adsorbed on the surface of the magnetite. The $M-O^{2-}$ union is thus weak, which causes the release of a metal ion (Fe^{3+} , Fe^{2+} , ...).

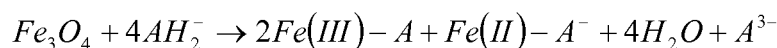
[0027] As a general rule, these mechanisms depend on the pH. The second mechanism has been seen to be prevalent in respect of the first.



[0028] The previous table shows how the magnetite is dissolved by means of citric acid.

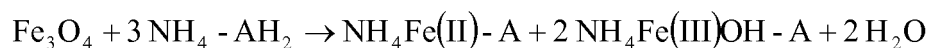
[0029] The reaction of dissolving by citric acid or by citrate ions can be written down as follows:

Equation 1



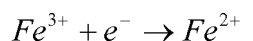
The proportion of AH_2^- citrate ions varies depending on the pH. From pH = 3.2 to pH = 4.8, this species is prevalent. The dissolution obtained by the combined action of the H^+ ions and the citrate; the optimum range for the dissolution must lie from pH = 3 to pH = 5. Ammonia can be added to obtain this pH. In an acid medium, the ammonia will start to form part of ammonium (NH_4^+) ions which will be associated with the citrate ions to form an ammonium citrate compound. The dissolution (equation 2) is very similar to the previous one.

Equation 2



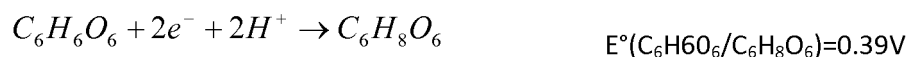
Apart from this, the ascorbic acid is a reducing agent. It reduces the Fe^{3+} ions to Fe^{2+} . The consumption of Fe^{3+} ions displaces the equilibrium of equation 2 to the right, improving the efficiency and yield of the process.

Equation 3

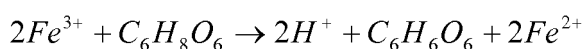


$$E^{\circ}(Fe^{3+}/Fe^{2+}) = +0.77V$$

Equation 4

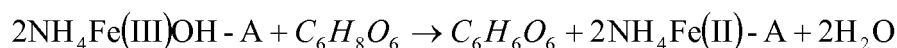


Equation 5



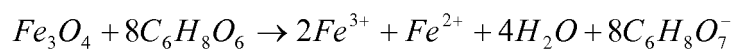
[0030] Equation 5 can also be written as follows:

Equation 6



[0031] The ascorbic acid is also able to dissolve magnetite (Equation 7).

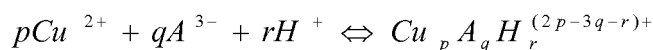
Equation 7



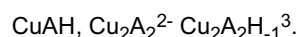
Influence of the presence of copper.

[0032] The citric acid has an important function as an agglutinant of the transition metal ions. The formation of compounds of Cu(II) citrate can be represented by the general equilibrium:

Equation 8

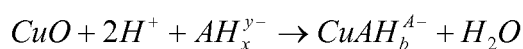


The predominant phases between pH 3 and 4 are as follows:



The citric acid can also be used for dissolving copper oxide (equation).

Equation 9



[0033] Tests have been made in order to verify the theoretical dissolving power of ascorbic and citric acids alone and in combination with copper. The results of these tests have proven that citric and ascorbic acids, alone or in combination,

would not have any power to dissolve the copper without the presence of magnetite.

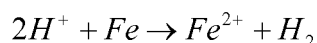
Corrosion reactions.

5 Actions of H^+ ions

[0034] H^+ ions are generated from the combination as in the following reaction.

10

Equation 10



This type of corrosion is limited when a corrosion inhibitor is used.

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Action of Fe^{3+} ions.

[0035] Fe^{3+} ions are produced through the dissolution of magnetite, and have the ability to oxidise iron (Equation 11: Corrosion reaction) and copper.

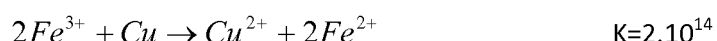
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Equation 11



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Equation 12



The Cu^{2+} turned into a solution could later be redeposited on the steels, possibly generating losses through corrosion.

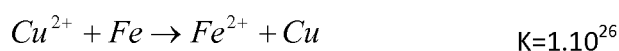
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Coppering

[0036] Coppering is when metal copper is deposited on a metal surface. The dissolved Cu^{2+} ions are released through the deposits being dissolved.

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Equation 13



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Citrate ions are commonly used in electrolytic baths for depositing conductive metal copper. The combination with the ions does indeed seem to favour copper depositing and improve the homogeneity of the deposit.

Function of ascorbic acid

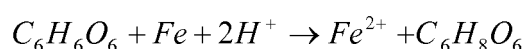
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[0037] As will be explained below, ascorbic acid reduces the Fe^{3+} ions in Fe^{2+} . The reduction of the amount of Fe^{3+} ions also implies that of Cu^{2+} ions in solution form (Equation 12), thus reducing the coppering phenomenon. As a result the addition of ascorbic acid should reduce corrosion.

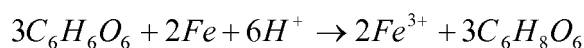
[0038] However, the product obtained from the oxidation of ascorbic acid by the Fe^{3+} ions (dehydroascorbic acid) can also generate corrosion.

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Equation 14



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Equation 15

Galvanic corrosion

[0039] In operating conditions the chemical condition of the water in the secondary circuit prevents free and galvanic corrosion. On the other hand, the dissolution of the deposits (mainly made up of magnetite) generated by chemical cleaning very slightly increases the possibility of galvanic corrosion. In this process the tubes made of the alloy used, with the trade name of "Inconel" and the stainless steel supports act as cathodes to the detriment of the low alloy steel or carbon steel compounds which then play the role of sacrificial anodes. The main factors influencing this type of corrosion are:

- o The nature of the electrolyte (reducing or oxidising medium) and its conductivity,
- o Polarisation: some products can slow down or halt corrosion reactions (e.g. corrosion inhibitors, corrosion products, etc.)
- o The relative surface area of the cathode in respect of that of the anode. The greater the surface area of the cathode in respect of that of the anode, the greater the galvanic corrosion will be.

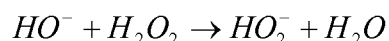
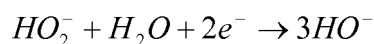
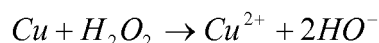
[0040] The main anodic reaction is as follows:

Equation 16

[0041] The main cathodic reactions are the same ones as the corrosion reactions mentioned in the previous paragraphs (Equation 10, Equation 11, Equation 12, Equation 13, Equation 14, and Equation 15).

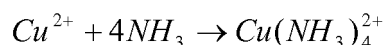
Decoppering phase

[0042] The decoppering phase has the aim of dissolving the metal copper liable to be redeposited in the acid phase. At first the hydrogen peroxide (H₂O₂) allows the oxidation of copper in the following reactions:

Equation 17**Equation 18****Equation 19****Equation 20**

[0043] In a second stage the dissolved Cu²⁺ ions are combined with the ammonia in the following reaction:

Equation 21



This compound is very stable for a pH > 9.5.

The ammonia has a combining function whilst the ammonium ion (resulting from the ammonium bicarbonate) has a function as a catalyst of the combination reaction.

Detailed description of the execution of the procedure according to the invention

[0044] The execution of the procedure being described comprises different stages which are numbered and explained below

[0045] The general procedure involves at least the following phases:

- Initial filling and testing of the system; guaranteeing the sealing of the system with mounting at temperature.
- Acid phase : the stage of dissolving the deposits of metal oxides (mainly iron)
- Emptying and rinsing: elimination of the solvent residues
- Decoppering phase: the stage of dissolving any copper possibly redeposited during the acid phase
- Final rinsing
- Final spraying and overall televisual examination.

Initial filling and testing of the system

[0046] The first chemical cleaning phase is filling the circulation loop assembly.

[0047] This stage is performed in two acts, filling up to just under the connections of the steam generator (GV) (loop/GV interfaces) and then up to the first target level before the injection of chemical reagents, in order to:

- Guarantee the complete sealing of the system
- Detect any possible leaks in the level of the connections on the circulation loop (flexible hoses, other connections and interfaces on the steam generator level).

[0048] It also enables verifying the proper operation of the auxiliary cleaning equipment (pumps, boiler, compressors, etc.), of the control systems and measuring systems.

[0049] The initial filling of the circuits (Auxiliary equipment and GV) will be done with demineralised water coming directly from the SED lines.

[0050] After the initial filling of the steam generator up to the first intended level, the boiler and the recirculation system are started up until the required temperature for the acid phase is reached through an external heating system made up of plate exchangers fed by a boiler located on the loop set in the outside of the reactor building.

[0051] The circulation loop is equipped with check valves. Anti-foaming agent will be added just before the injection of the reagents of the acid stage.

Phase for dissolving the deposits: acid phase

[0052] The aim of this first phase is to partially dissolve the deposits of oxides made up mainly of magnetite, present in the steam generator on the level of the separator plates and in the free part of the tubes, as well as obstructing the passages of the four-leaved supports of said tubes.

[0053] The operating action procedure according to the invention has two variants:

- For a load ≤ 30 g/l : procedure A
- For a load > 30 g/l : procedure B

[0054] The following table indicates the conditions and physical-chemical parameters of the acid phase for each of the variants, as an example.

	Reference values - Operating ranges	
	<i>PROCEDURE A 6 to 35g/l</i>	<i>PROCEDURE B 25 to 50g/l</i>
Amount of deposits (<0.5 to 8% of copper)		
Citric acid (% mass)	0.5-10	
Ascorbic acid (% mass)	0.3-5	0.2 ; 4
Formic acid (% mass)	0-6%	
Inhibitor (% mass)	0.5 ; 1	
Anti-foaming agent (% mass)	0.2 [0.2; 0.5]	
Initial pH	1-4.5	
Temperature (°C)	25-70	20-65
Duration (upper drainage) (from the start of the injection of the acid mixture)	12h	
Maximum duration (including drainage)	≤24h o [Fe _{tot}] > predetermined threshold + 4h	
Recirculation speed (m/s)	0 to 1.1	
Recirculation outlet (m ³ /h)	0 to X	
Bubbling nitrogen (Nm ³ /h)	10 to 80	
Target level	Over the exchanger tube dome	

[0055] The formic acid can complement the ascorbic acid or the mixture of citric acid with ascorbic acid, especially in the case of the absence of copper in the alloys used.

[0056] Another criterion of the end of phase or control alert for end of phase is when a certain threshold in the amount of iron obtained on the electrolyte is reached.

[0057] This phase takes place immediately after the sealing tests, the heating of the solution circulating in the steam generator and the nitrogen bubbling. At the time of simultaneous injection of the mixture of concentrated acids and the corrosion inhibitor at the recirculation pump level the loop including the steam generator is filled with water to the level of the recirculation pump, and demineralised water is added with an anti-foaming agent. At the start of injection the temperature of the solution is around 25 and 70°C or 20 and 65°C depending on the procedure applied.

[0058] The simultaneous injection of the mixture of citric-ascorbic acids and the inhibitor is done through their respective injection pump on the suction level of the recirculation pumps.

[0059] Ammonia is injected in order to adjust the pH to the required pH level, which is done in the same way as that of the mixture of acids and inhibitor, i.e. at the suction level of the pumps.

[0060] The solvent is inserted at the top of the steam generator with a burst jet system located over the bundle of tubes.

[0061] The solution recirculates from the top of the steam generator downwards. In parallel, the nitrogen bubbling is done by means of injection cannula located at the bottom of the steam generator.

[0062] The temperature is maintained around the reference temperature for the entire phase.

[0063] Water is added until the minimum level of the acid phase is reached.

[0064] Homogenising the solution is considered to take 20 minutes depending on the speed of recirculation and the nitrogen bubbling. This duration was determined by extrapolating the results of the tests performed with the aid of a propagation model with a proven recirculation flow of 30 m³/h and a propagation flow of 30Nm³/h.

[0065] The physical-chemical parameters are monitored (at intervals of from half to one hour for the samples) in order to monitor the evolution of the acid phase and to ensure its proper development until one of the criteria for the end of the phase is attained.

[0066] The end of phase criteria are as follows:

- Total iron > predetermined threshold: phase criterion depending on the concentration of total dissolved iron, that is, a known amount of magnetite and its associated corrosion, or
- A duration of 20h

[0067] Hence, the maximum length of this phase is 24 hours, including the previous filling and later emptying times.

[0068] The analysis of the chemical parameters according to the previous table will be done by a semi-automatic dispensing method (with the trade name of Titrando). During this phase only the temperature and the flow will be piloted

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through the heating system and the pumps respectively. The supervision of corrosion will be done continuously as in the following table.

Parameters monitored	Justification
Concentration of total dissolved iron (<i>sample</i>)	Monitoring the chemical end of phase criterion and measuring the efficiency of dissolution
pH (<i>sample</i>)	Adjustment of the pH and verification of the consistency with the observations of the development tests and certification of the procedure
Flow (<i>continuously measured</i>)	- Maintenance of the flow and guarantee that there is no phase lag in respect of the maximum recirculation speed - checking the duration of the injections as well as of the required injected volume to find out the initial concentrations of the reagents in the steam generator
Level in the steam generator (<i>continuously measured</i>)	- checking the level in the steam generator and guaranteeing that the level is properly maintained - guarantee that there is no contamination of the other circuits and auxiliary circuits
Duration (<i>continuously measured</i>)	End of phase criterion
Temperature (<i>continuously measured</i>)	Checking the harmlessness and efficiency of the phase
System for monitoring the corrosion (<i>continuously measured</i>)	- estimation of the corrosion in real time - verification of whether the limit for action of the corrosion monitoring system is attained
Concentration of ascorbic acid (<i>sample</i>)	Monitoring the maintenance of the reduction medium
Concentration of dissolved copper (<i>sample</i>)	- Monitoring the dissolved copper and indirectly the redepositing of copper
Concentration of dissolved Fe III (<i>sample</i>)	For information purposes for monitoring the efficiency of the ascorbic acid

[0069] This means that the monitoring of the free and galvanic corrosion on line can be guaranteed by means of the corrosion monitoring system. Corrosion test pieces will be located inside the steam generator and in the connected circuits.

[0070] A limit is defined for activating the system for monitoring corrosion (early emptying) in order to guarantee the harmlessness of the process in the event of there being excessively high corrosion kinetics. This limit could be reviewed after the first stage in the phase.

[0071] On-line monitoring of corrosion would complement the supervision of the total concentration of dissolved iron enabling estimating the efficiency and corrosion in real time and guaranteeing the procedure. It enables stopping depending on the amount of magnetite dissolved and/or of the corrosion.

Rinses

[0072] In order to optimise the volume of effluents and the duration of the rinses, the rinsing stage is made up of 1 to 3 low volume rinses (filling the steam generator at the level of the dividing plate 1) followed by a full volume rinse (filling level of the steam generator over or equal to that of the acid stage).

[0073] Conditions for starting up:

- Small volume rinses :

- ✓ Chemical: demineralised water
- ✓ Minimum level: but over the connection to the steam generator

- Full volume rinse

- ✓ Chemistry: demineralised water with pH adjustment over 9 with ammonia in order to neutralise any possible residues from the acid stage

- ✓ Bubbling with nitrogen
- ✓ Minimum level: equal or over the level of the acid stage

[0074] Parameters monitored:

- Level in the steam generator,
- Only for rinsing large volumes :

o pH

o end of phase criterion: pH stabilised and ≥ 8

Execution of optional spraying

[0075] After the rinsing in the acid stage an intermediate spraying stage can be performed in order to eliminate the sludges found in the waste at the bottom part of the steam generator, in order to prevent the structural embrittlement and redepositing of magnetite through gravity after the acid phase. This means an optimum decoppering effectiveness can be guaranteed. In the event of spraying being carried out a televisual examination will be performed.

Decoppering stage

[0076] The decoppering stage will take place only when the cleaning is done on alloys with copper content.

[0077] The solvent for decoppering has the aim of eliminating any copper that could be deposited during the stage for dissolving the deposits of oxides in the internal parts of the steam generator, and more specifically on the tubes, as well as part of the copper present in the deposits. In this stage a water solution of ammonia is added, and possibly also of ammonium bicarbonate, as well as a strong oxidiser, such as hydrogen peroxide.

[0078] In order to optimise the efficiency of the decoppering operation and to control the temperature, the decoppering phase is performed in two stages.

[0079] During the first stage the injection of the ammonium/ammonium bicarbonate mixture and hydrogen peroxide is done only at the bottom of the steam generator between lower connections. The recirculation takes place between these connections as a by-pass.

[0080] The steam generator is filled continuously with the ammonia/ammonium bicarbonate mixture and demineralised water while the hydrogen peroxide is injected very slowly in order to control the temperature as far as possible.

[0081] When the solution has reached the low intermediate level, the injection of the decoppering mixture starts to be done at the top of the steam generator. The recirculation then takes place from the top downwards. Only the injection of hydrogen peroxide takes place in parallel through the upper and lower part of the steam generator, for example with a distribution of affluent of 30 and 70% respectively (in flow).

[0082] The following table shows the execution conditions, according to a non-limiting form of embodiment:

	Minimum values	Operating ranges
Parameters	With intermediate spraying	Without intermediate spraying
Amount of deposits (<0.5 to 8% copper)	6 to 50g/l	
Ammonia or Ammonium Hydroxide (water solution of ammonia) (g/l)	5-20	
Ammonium bicarbonate (g/l)	0-10	
Hydrogen peroxide (% mass)	0.1-0.5	
pH	≥ 8.0	
Temperature (°C) (initial, before the first injection of hydrogen peroxide)	10-75	
Duration (h) (t_0 represents the injection of hydrogen peroxide. The duration means the duration between t_0 and emptying)	≥ 8 [8 ; 18] (including the rinse)	≥ 9 [9 ; 18]

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(continued)

	Minimum values	Operating ranges
Parameters	With intermediate spraying	Without intermediate spraying
Recirculation flow(m ³ /h)	0 to X	
Air bubbling (Nm ³ /h)	[10; 80]	
Minimum level	Niv2 ≤ Niv3 < dome of the exchanger	

Stage 1

[0083] Injection and circulation in bypass through the steam generator until the minimum intermediate level is attained

Stage 2

[0084] Parallel injection from the top of the steam generator downwards until the lower minimum level is attained (Niv3)

[0085] The physical-chemical parameters are monitored (at intervals of half to one hour for the samples) to monitor the evolution of the decoppering stage and ensure its proper development until one of the end of phase criteria is attained.

[0086] End of phase criteria (upper drainage):

- with intermediate spraying: minimum duration = 8h
- **without** intermediate spraying : minimum duration = 9h

[0087] The duration of the decoppering stage will be adapted depending on the level of scale and the amount of copper in each location.

Parameters monitored	Justification
Concentration of dissolved copper (<i>sample</i>)	- monitoring the efficiency of the decoppering phase (copper from the coppering or from the copper found in the deposits) - verification of the stability of the decoppering stage and maintenance of its efficiency
pH (<i>sample</i>)	- verification of the stability of the pH and particularly for the pH to be ≥ 8 throughout the phase
Temperature (<i>continuously measured</i>)	- a determining parameter for the first injection of hydrogen peroxide and which enables immediately managing the injection to reduce the effect of exothermal reaction and optimising the efficiency of decoppering
Flows (<i>continuously measured</i>)	- governing the durations of injection as well as the volumes injected required to learn the initial concentrations of the reagents in the steam generator
Level in the steam generator (<i>continuously measured</i>)	- verification of the adjustment to the level in the steam generator and guarantee that the minimum level is attained - guarantee that there is no contamination in the dome of the exchanger and auxiliary circuits
Duration (<i>continuously measured</i>)	End of phase criterion
System for monitoring the corrosion (<i>continuously measured</i>)	Estimation of corrosion in real time
Concentration of dissolved iron (<i>sample</i>)	For information purposes

[0088] Furthermore, only for announcement purposes, the free and galvanic corrosion are monitored on line by means

of the corrosion monitoring system. The same corrosion test pieces which have been subjected to the acid phase will be reused (the test pieces removed from the steam generator during the intermediate spraying stage, if this has been performed).

5 Rinses

[0089] To optimise the volume of the effluents and limit the duration of rinses, the rinsing stage consists of from 1 to 3 low volume rinses, followed by a full volume rinse (filling the steam generator from the top over the low connections), followed by a full volume rinse (filling level of the steam generator equal to or over that of the decoppering phase).

10 **[0090]** Execution conditions:

- low volume rinse

✓ Chemical: SED water

15 ✓ Low level : over the low connections of the steam generator

- Full volume rinse

✓ Chemical: SED water,

20 ✓ Recirculation over ion-exchange resins and air bubbling

✓ Low level : $Niv4 \geq Niv3$

[0091] Parameter monitored:

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- Level in the steam generator
 - Only for large volume rinsing:

o End of phase criterion : conductivity verified $< 30 \mu S/cm$ at $25^\circ C$ (usage of ion-exchange resins to attain this objective)

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Final spraying and overall televisual examination

[0092] After the final rinse a final spraying is performed followed by a full televisual examination.

35 **[0093]** The characteristics of the liquid effluents as well as the estimated amounts of the liquid and gaseous effluents will be determined at the outlet of the first stage in each series.

[0094] The gaseous species which could be issued during execution of the procedure are:

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- During the acid phase: hydrogen, ammonia, carbon dioxide and nitrogen
 - During the decoppering phase: ammonia, carbon dioxide and dioxygen
 - During the rinses: ammonia

[0095] At the outlet of the qualification of the process the species to be covered by monitoring by an accredited laboratory will be determined during the on-site execution in order to ensure, amongst others, that the amount of ammonia rejected is under 50 Kg per intervention.

45 **[0096]** The volumes of liquid effluents will range from about 1500 to 2200 m³ depending on the type of power station being operated on.

Evaluation of the corrosion efficiency

50 **[0097]** After the execution of the procedure, in order to appraise conformity according to efficiency and harmlessness criteria the following will be estimated:

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- The amount of total deposits eliminated: the sum of the amount estimated from the chemical data (iron, copper concentration, etc.) during the set of phases in the procedure, added to the amount eliminated through spraying and to the ones recovered in particular filters installed on the line
 - The corrosion of the test pieces located in the steam generator which will enable evaluating, through the loss of mass at the end of the procedure, the level of corrosion undergone by the internal parts of the steam generator and connected circuits and allow the requalification of the main secondary circuit.

Claims

1. A chemical cleaning procedure for heat exchangers such as steam generators at PWR-type thermonuclear power plants in which the steam generator is a heat exchanger made up of a set of tubes from the primary circuit, these tubes being separated by separation plates, said tubes and said plates being coated when in use with deposits adhering to these of materials from erosions, corruptions and impurities in the secondary circuit, these materials being particularly formed of metals and metal oxides such as magnetite and metals such as copper, this procedure comprising two main stages, a first phase of eliminating the metal oxides and in the event of the cleaning being done on materials containing copper, a second phase for decoppering and eliminating any copper compounds, **characterised in that:**

In the first phase a water solution is inserted in the steam generator with the following reagents:

- Citric acid, 0.5-10% in mass
- Ascorbic acid 0.3-5% in mass
- The process is carried out at a temperature of 20°C-70°C
- And the pH for the process starts at values of from 1 to 4.5

2. A chemical cleaning procedure for heat exchangers, according to claim 1, **characterised in that** this also comprises the addition of formic acid up to 6%.
3. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 2, **characterised in that** this also comprises the addition of a corrosion inhibitor.
4. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 3, **characterised in that** this also comprises the addition of an anti-foaming agent.
5. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 4, **characterised in that** this also comprises the injection and bubbling of nitrogen as a means for homogenising the reagents and sweeping off the dissolved metal compounds and for maintenance of the reducing nature of the solution.
6. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 5, **characterised in that** the first phase lasts for at most 24 hours.
7. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 6, **characterised in that** this comprises monitoring the concentration of total iron and monitoring the procedure from said concentration.
8. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 7, **characterised in that** the first phase of eliminating metal oxides is done dynamically in a continuous cycle.
9. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 8, **characterised in that** a water solution comprising the following reagents is inserted in the second phase for decoppering and copper compounds:

- Ammonia or ammonium hydroxide 5-20 g/l
- Ammonium bicarbonate 0-5 g/l
- Hydrogen peroxide 0.1-0.5% in mass
- The process is carried out at a temperature of 10°C-75°C
- The pH of the process is kept at values > 8.

10. A chemical cleaning procedure for heat exchangers, according to claim 9, **characterised in that** the mixture of the water solution of ammonia and ammonium bicarbonate is done initially, and because hydrogen peroxide is added very slowly depending on the resulting temperature of the solution.
11. A chemical cleaning procedure for heat exchangers, according to any of claims 9 to 10, **characterised in that** the decoppering stage lasts for at least 4 hours and at most 24 hours including the rinsing.
12. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 11, **characterised in that** the

second decoppering stage is performed dynamically in a continuous cycle.

5 13. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 12, **characterised in that** this comprises one or several rinsing stages after the acid phase, adjusted to a basic pH.

10 14. A chemical cleaning procedure for heat exchangers, according to any of claims 1 to 13, **characterised in that** this comprises a rinsing stage after the decoppering stage for which the rinsing solution is filtered through ion-exchange resins in order to reduce conductivity until the required conductivity is attained.

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INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER

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ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

F28G F22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

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X	US 2002/196891 A1 (ROOTHAM MICHAEL W [US] ET AL) 26 December 2002 (2002-12-26) paragraph [0001] paragraph [0011] - paragraph [0013]; claims 2,3,4 -----	1
X	WO 2005/097689 A1 (DOMINION ENG INC [US]; VARRIN JR ROBERT D [US]; KANEDA SOTARO [JP]; SA) 20 October 2005 (2005-10-20) claim 14 ----- -/-	1



Further documents are listed in the continuation of Box C.



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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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