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(54) **An application technique for the decontamination of nuclear reactors**

(57) A method of applying a decontaminating reagent comprising a one-electron reducing agent based on V^{II} or Cr^{II} in combination with a complexing agent to the cooling system of a nuclear reactor or to a decontamination facility, which method comprises:

- (i) maintaining the V^{II} or Cr^{II} ion either in solution under an inert atmosphere in a container made of or lined with an inert material or as a solid salt under an inert atmosphere;
- (ii) preparing a solution of the complexing agent and removing oxygen therefrom; and
- (iii) mixing the ingredients from steps (i) and (ii) either *in situ* in the cooling system of the nuclear reactor or in the decontamination facility, or mixing (i) and (ii) prior to application to the cooling system of the nuclear reactor or to the decontamination facility under conditions whereby no substantial decomposition of the so-formed decontamination reagent occurs.

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SPECIFICATION

An application technique for the decontamination of nuclear reactors

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The present invention relates to an application technique for the decontamination of the cooling system or components associated with the cooling system of water-cooled nuclear reactors, or other

10 contaminated plant items, using the particular chemical process which is described in our co-pending British Patent Application No. 80.00584.

The construction materials of water-cooled nuclear reactors are corroded by the aqueous coolant and small amounts of their constituent elements are released into the coolant. These constituent elements become neutron activated in the reactor core and are ultimately deposited in the form of their oxides on the vessel and pipework surfaces throughout the coolant circuits, giving rise to large radiation dose rates in the circuit. It is desirable to remove these oxide deposits to reduce the radiation dose rates prior to man access.

Our co-pending British Patent Application No. 25 80.00584 describes and claims a process for decontaminating the cooling system or a component associated with the cooling system of a water-cooled nuclear reactor, or other contaminated plant items, which process comprises circulating a decontaminating reagent at a pH below 7.0 through the cooling system of the reactor, or contacting a component associated with the cooling system or containing other contaminated plant items with a decontaminating reagent at a pH below 7.0, the decontaminating reagent comprising a one electron reducing agent based on V^{II} or Cr^{II} in combination with a complexing agent which is thermally and radiolytically stable at the operating pH. In this process, the radioactive oxides dissolve and a solution is obtained which is suitable for treatment by ion exchange to remove both the radioactive ions and the decontaminating chemicals from the system being cleaned. In this process the decontaminating reagents are circulated in the cooling system of the reactor, or contacted with the component to be cleaned in a suitable decontamination facility.

Traditional methods of reactor decontamination employ mixtures of chelating acids which are stable both individually and when mixed in aqueous solution. These acids can therefore be premixed as a solution or slurry and pumped into the circuit to be cleaned. The chemicals to which the present technique relates are, both individually and when mixed, sensitive to both air and the presence of metal surfaces and require special handling techniques if the decontamination process is to be successfully accomplished.

An example of the type of reagent that has previously been used in the decontamination of nuclear reactors is a mixture of citric and oxalic acids. Those chemicals are solids which are stable in air both separately and when mixed together. The mixture can therefore be stored for long periods of time, often years, with no ill effect and it can be dissolved in water in any suitable vessel at any time

prior to injection into the reactor or decontamination facility. Stainless steel is the material most commonly used for the preparation and storage of these reagent solutions.

70 The decontaminating reagents described in our co-pending patent application No. 80.00584 consist of two essential components: a metal ion in a low oxidation state, such as chromium (II) or vanadium (II), and a complexing agent, such as picolinic acid or bipyridyl. The complex formed when the two components are brought together performs the necessary reduction to bring about dissolution of the radioactive oxides. These reagents are by certain specialists in this field referred to as "LOMI" reagents (low oxidation state metal ion reagents).

Although the complexing agent in these reagents is usually a stable chemical, capable of prolonged storage, we have found that this does not apply either to the low oxidation state metal ion, in solution or as a solid salt with the appropriate counterion, or the complex formed between the metal ion and the complexing agent. It will be appreciated by those skilled in the art that these reagents are sensitive to oxygen, and must therefore be used under an inert atmosphere. However, we have found that even when oxygen is excluded from these reagents, decomposition of the reducing agent is quite rapid in the presence of materials capable of catalysing the reduction of water by the metal ion. For example, we have found that concentrated solutions of vanadium (II) formate lose much of their reducing ability after only one day in contact with stainless steel. Similarly, dilute solutions of the complex formed between vanadium (II) and picolinic acid rapidly lose their capacity to dissolve oxides when heated in the presence of stainless steel. Other "LOMI" reagents decompose on storage even in vessels made of inert materials such as glass; for example, solutions of vanadium (II), or chromium (II), with the complexing agents ethylenediamine-tetra-acetic acid, or nitrilotriacetic acid, are only stable for a few hours when heated.

Accordingly, the present invention provides a method of applying a decontaminating reagent comprising a one-electron reducing agent based on V^{II} or Cr^{II} in combination with a complexing agent to the cooling system of a nuclear reactor or to a decontamination facility which method comprises:

- (i) maintaining the V^{II} or Cr^{II} ion either in solution under an inert atmosphere in a container made of or lined with an inert material or as a solid salt under an inert atmosphere;
- (ii) preparing a solution of the complexing agent and removing oxygen therefrom; and
- (iii) mixing the ingredients from steps (i) and (ii) either *in situ* in the cooling system of the nuclear reactor or in the decontamination facility, or mixing (i) and (ii) prior to application to the cooling system of the nuclear reactor or to the decontamination facility under conditions whereby no substantial decomposition of the so-formed decontamination reagent occurs.

The complexing agent which is used in the present invention must in use of the reagent, maintain all metal ions present in solution at the operating pH. It

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is beneficial if the complexing agent promotes spin pairing when used with Cr^{II} so that the Cr^{II} ion will undergo rapid outer sphere electron transfer reactions, and should not lower the redox potential of the system to a value such that the rate of water reduction can compete with the dissolution process. It will also be appreciated by those skilled in the art that the complexing agent must have an adequate radiation stability. Examples of suitable complexing agents are ethylene diamine tetraacetic acid, citric acid, picolinic acid, 2,2'-bipyridyl, histidine, nitrilotriacetic acid and 2,6-dicarboxy pyridine. However, 2,2'-bipyridyl does show some sensitivity to radiation and it is therefore not suitable for use in decontaminating reagents for use in in-core regions, although it is suitable for use for component and out of core decontaminations where radiation doses are 10⁴ to 10⁵ times smaller.

Specific examples of the decontaminating reagents for use in the invention are a one-electron reducing agent based on V^{II} in combination with picolinic acid and a one-electron reducing agent based on Cr^{II} in combination with bipyridyl.

The concentration of metal ion used in the decontaminating reagents is preferably 10⁻³ to 2M, more preferably 10⁻³ to 10⁻² M. The molar concentration of the complexing agent is generally from 3 to 10 times the molar concentration of V^{II} or Cr^{II}. When formate or acetate is present as the counterion in the decontamination reagents they are generally employed at a molar concentration of from 5 to 20 times the molar concentration of V^{II} or Cr^{II}.

In carrying out the method of the invention the V^{II} or Cr^{II} metal ion is stored and transported either in solution under an inert atmosphere and in a container made or lined with an inert material, such as glass or plastic, or as a solid salt under an inert atmosphere. This component is combined with the complexing agent in such a manner that the complex reagent thus formed is not destroyed before performing the decontamination, by reaction with oxygen, or by the catalytic effect of metal surfaces in promoting spontaneous reaction with water. A solution of the complexing agent, and any other reagent required for the control of pH, or a surfactant, is prepared and oxygen is removed therefrom for example by sparging with an inert gas such as nitrogen. Hydrazine may be added to solution to ensure complete removal of oxygen. This solution is then brought to the desired temperature, for example 80°C. The V^{II} or Cr^{II} metal ion is then added to the solution so prepared, using an atmosphere of inert gas, in one of three ways. The solution described above may be introduced into the cooling system of the reactor, or into the decontamination facility, and circulated prior to the introduction of the V^{II} or Cr^{II} metal ion in solution. The complex reagent is thus formed directly *in situ*. The solution described above may be introduced into the reactor or decontamination facility while the V^{II} or Cr^{II} metal ion, in solution also, is simultaneously introduced so that the complex reagent is formed in the pipework whilst flowing into the reactor or decontamination facility. Alternatively, the solution described above may be prepared in a vessel made of or lined with, an inert

material such as glass or plastic, and the V^{II} or Cr^{II} metal ion may then be added either in solution or as a solid salt, and mixed with the complexing agent to form the required decontamination reagent prior to injection into the reactor under conditions whereby no substantial decomposition of the decontamination reagent occurs, for example by mixing the reagents in a vessel made of or lined with an inert material.

When the decontamination reagent to be used is a complex such as vanadium (II) with picolinate, any of these three methods could be applied. When the reagent is liable to undergo spontaneous reaction with water, for example the chromium (II) nitrilotriacetate complex, then the third method described above would be least satisfactory. The first method will result in the most efficient use of the decontamination reagent with any of the reagents described.

The concentration of the "LOMI" reagent may be followed by measuring the visible or ultra-violet spectrum of the solution during the course of the decontamination, either by periodic removal of samples for analysis under air-free conditions, or by the continuous bleeding of solutions through a suitable colourimeter or spectrophotometer.

Further addition of the reduced metal ion may be made during the course of the decontamination, if required. This may be necessary if the amount of oxide to be removed is greater than anticipated, or if significant decomposition of the "LOMI" reagent occurs. Addition of further complexing agent may also be required. The methods for such additions are the same as in the initial injection of reagents.

Under conditions where the decontaminating reagent experiences a strong field of radiation, e.g. in the core of a pressurized water reactor, some "LOMI" reagents are regenerated by reactions involving formic acid, as described in our co-pending Patent Application No. 80.00584. There may therefore be the need to add further formic acid. This is injected via the same system as used for the reduced metal ion solution, either as formic acid directly or as a solution of an appropriate salt, such as lithium formate or ammonium formate.

After the reaction has been circulated through the system being cleaned it is removed from the system. The simplest method of removal is to drain the reagent from the system replacing it by clean water and to rinse the system several times. However, this may lead to unacceptable quantities of radio-active waste solution and the preferred method of treatment is therefore to pass the solution through cation and anion exchange resins which remove both the radio-active ions and the decontaminating reagent and provide all the waste in a convenient solid form.

Example

A reagent based upon vanadium (II) (as the low oxidation state metal ion) and picolinic acid (as the complexing agent) was used to decontaminate the south circuit of the Steam Generating Heavy Water Reactor (SGHWR) at Winfrith Heath, Dorset, U.K.

For this exercise, vanadium (II) formate was produced in the form of a solution having the approximate composition vanadium (II) ion 0.2M

and formate/formic acid 2M in water. The solution was produced by the direct electrolysis of V_2O_5 in formic acid as described in our co-pending patent application No. 80.00584. The solution was transferred to and stored in commercially available high density polyethylene drums each having a capacity of 220 litres. The drums were thoroughly purged with an inert gas before filling. A total volume of 1,700 litres was produced. The vanadium (II) formate solution was transported to the reactor site and stored prior to use. The period of storage was up to two weeks.

Picolinic acid was obtained as the pure solid (400kg) and was transported to the reactor site without special measures.

At the reactor site the picolinic acid was dissolved in 30,000 litres of water in a stainless steel reagent tank. The solution was heated to 80°C by steam and the solution was freed of oxygen by the passage of oxygen-free nitrogen from sparge-pipes through the solution. In order to ensure that the reagent formed in the reactor was at the correct pH value for the decontamination, it was necessary to add sodium hydroxide solid (125kg) to the tank liquor. Mixing of the reagents was ensured by nitrogen and stream sparging and also by pumping the reagent around a closed loop.

The reactor was made ready for decontamination by filling the circuit to the maximum level and injecting hydrazine with the reactor coolant pumps running until a stable value of concentration was obtained (the hydrazine removes residual oxygen in the reactor circuit). The reactor pumps were then stopped and the coolant was partially drained to make space for the decontaminant solution. The reactor water was displaced with oxygen-free nitrogen.

Injection of the decontaminant solution then took place. The vanadium (II) formate solution was pumped from the storage drums (the solution in the drums being displaced by oxygen-free nitrogen) and the picolinic acid/sodium hydroxide solution from the make up tank, and the two streams mixed as they entered the reactor pipework leading to the stream drum. The rate of injection of each of these chemicals was monitored to ensure that injection took place evenly, and that the vanadium (II) formate addition was complete before the picolinic acid/sodium hydroxide addition in order to allow for flushing of the injection pipework with the latter solution.

Once injection was complete the reagent tank was isolated by closing the appropriate valves, and circulation of the decontamination reagent was effected by operation of the reactor coolant pumps.

When decontamination was complete the circuit was partially drained and refilled repeatedly until the coolant water had the appropriate chemical constitution.

The efficiency of these arrangements for the production of the decontaminating solution in the reactor was confirmed by spectrophotometric determination of the vanadium (II) picolinate complex in samples of reactor coolant water taken immediately after injection of the reagent and prior to circulation.

About 23kg of metal oxide deposits were dissolved

by the reagent during the decontamination which is equivalent to that expected for the amount of reagent added.

70 CLAIMS

1. A method of applying a decontaminating reagent comprising a one-electron reducing agent based on V^{II} or Cr^{II} in combination with a complexing agent to the cooling system of a nuclear reactor or to a decontamination facility, which method comprises

- (i) maintaining the V^{II} or Cr^{II} ion either in solution under an inert atmosphere in a container made of or lined with an inert material or as a solid salt under an inert atmosphere;
- (ii) preparing a solution of the complexing agent and removing oxygen therefrom; and
- (iii) mixing the ingredients from steps (i) and (ii) either *in situ* in the cooling system of the nuclear reactor or in the decontamination facility, or mixing (i) and (ii) prior to application to the cooling system of the nuclear reactor or to the decontamination facility under conditions whereby no substantial decomposition of the so-formed decontamination reagent occurs.

2. A method as claimed in claim 1 wherein in step (iii) the solution of the complexing agent is introduced into the cooling system of the nuclear reactor or into the decontamination facility prior to the addition of the V^{II} or Cr^{II} ion in solution to form the decontaminating reagent *in situ*.

3. A method as claimed in claim 1 wherein in step (iii) the solution of the complexing agent and the V^{II} or Cr^{II} ion in solution are introduced simultaneously into the cooling system of the nuclear reactor or into the decontamination facility to form the decontaminating reagent *in situ*.

4. A method as claimed in claim 1 wherein in step (iii) the solution of the complexing agent and the V^{II} or Cr^{II} ion in solution are mixed in a vessel made of or lined with an inert material prior to injection into the cooling system of the nuclear reactor or into the decontamination facility.

5. A method as claimed in any one of the preceding claims wherein in step (i) the V^{II} or Cr^{II} ion is maintained in a container made of or lined with glass or plastic.

6. A method as claimed in any one of the preceding claims wherein in step (ii) oxygen is removed from the solution of the complexing agent by sparging with an inert gas.

7. A method as claimed in claim 6 wherein the inert gas is nitrogen.

8. A method as claimed in any one of the preceding claims wherein the complexing agent is ethylene diamine tetracetic acid citric acid, picolinic acid, 2,2'-bipyridyl, histidine, nitrilotriacetic acid or 2,6-dicarboxy pyridine.

9. A method as claimed in any one of the preceding claims wherein the decontaminating reagent comprises a one-electron reducing agent based on V^{II} and picolinic acids as the complexing agent.

10. A method as claimed in any one of the preceding claims wherein the decontamination reagent comprises a one-electron reducing agent based

on Cr^{II} and bipyridyl or nitrilotriacetic acid as the complexing agent.

11. A method as claimed in any one of the preceding claims wherein the concentration of the one-electron reducing agent based on V^{II} or Cr^{II} is in the range of from 10⁻³ to 2M.

12. A process as claimed in claim 11 wherein the concentration of the one-electron reducing agent based on V^{II} or Cr^{II} is in the range of from 10⁻³ to 10⁻²M.

13. A method as claimed in any one of the preceding claims wherein the molar concentration of the complexing agent is from 3 to 10 times the molar concentration of V^{II} or Cr^{II}.

14. A method as claimed in any one of the preceding claims wherein the formate or acetate is present as a counterion at a molar concentration of from 5 to 20 times the molar concentration of V^{II} or Cr^{II}.

15. A method as claimed in claim 14 wherein formate is present as the counterion, in which process the low oxidation state V^{II} of vanadium or the low oxidation state Cr^{II} of chromium is regenerated by radiation during the decontamination process and additional formic acid or a salt thereof is introduced into the cooling system of the nuclear reactor or into the decontamination facility.

16. A method as claimed in claim 1 substantially as hereinbefore described with reference to the Example.