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(54) Title: INCREASE OF EFFECTIVENESS AND EFFICIENCY IN THE OXIDE REMOVAL

(57) Abstract: The present invention relates to a method of decontaminating metal surfaces in a cooling system of a nuclear reactor, wherein the metal surfaces are coated with a solid metal oxide layer including radionuclides.

INCREASE OF EFFECTIVENESS AND EFFICIENCY IN THE OXIDE REMOVAL

Introduction

The present invention concerns a method of decontaminating metal surfaces in a cooling system of a nuclear reactor, wherein the metal surfaces are coated with a solid metal oxide layer including radionuclides.

When a nuclear reactor is operated, metal ions are released from these metal surfaces of the cooling system and transported into the coolant. Some of the metal ions are activated to form radioisotopes when passing the reactor core. A portion of the metal ions and radioisotopes is removed by the reactor water clean-up (RWCU) system during operation of the reactor. Another portion is deposited on the metal surfaces inside the reactor cooling system, and is later incorporated into metal oxide layers growing on the metal surfaces. Through the incorporation of radionuclides, these oxide layers become radioactive.

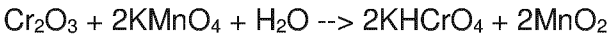
The removal of the radioactive oxide layers is required to reduce the level of personnel radiation exposure prior to carrying out inspection, maintenance, repair and dismantling procedures on the reactor cooling system

Depending on the type of alloy used for a component or system, the metal oxide layers contain mixed iron oxides with divalent and trivalent iron as well as other metal oxide species including chromium(III) and nickel(II) spinels. Especially the oxide deposits formed on the metal surfaces of the steam generator tubes may have a high chromium(III) or nickel(II) content which makes them very resistant and difficult to remove from the metal surfaces.

A number of chemical procedures have been described to remove metal oxide layers containing radioactive corrosion products from metal surfaces in the cooling system of a nuclear reactor, suitably during reactor operation, which requires rather mild conditions, for example low oxidation-state metal ion (LOMI) decontamination, Canadian decontamination and remediation process (CANDEREM), or chemical oxidation reduction decontamination (CORD).

CORD, for example, is a well-known decontamination process using permanganate as oxidation agent and oxalic acid as reducing agent. Accordingly, considering the specific oxides formed and their chemical and physical properties, several phases are typically part of such a treatment cycle for the chemical removal of oxide layers and trapped radioisotopes from metal surfaces in cooling systems. Thereby, a treatment cycle is typically performed more than once and a specific phase as part of the treatment cycle may be performed once or a plurality of times.

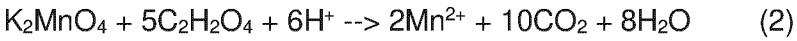
One early phase, typically called oxidation step, comprises the oxidation of chromium(III) oxide with potassium permanganate to solubilize chromium(VI) ions under acidic conditions, e.g. in the presence of nitric acid:



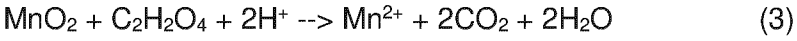
$$Cr_2O_3 + 2KMnO_4 + H_2O \dashrightarrow 2KHCrO_4 + 2MnO_2 \quad (1)$$

Instead or in addition to the phase above, the oxidation of chromium(III) oxide with potassium permanganate to soluble chromium(VI) ions and insoluble manganese(IV) oxide may be performed under alkaline conditions, e.g. in the presence of potassium hydroxide.

A subsequent phase, typically called reduction step, comprises the addition of a reducing agent such as oxalic acid to destroy any excess permanganate and convert insoluble manganese(IV) oxide into soluble manganese(II) salts under acidic conditions:



$$K_2MnO_4 + 5C_2H_2O_4 + 6H^+ \dashrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \quad (2)$$



$$MnO_2 + C_2H_2O_4 + 2H^+ \dashrightarrow Mn^{2+} + 2CO_2 + 2H_2O \quad (3)$$

In another subsequent phase, typically called the (actual) decontamination step or the dissolution step, the chromium depleted oxides, in particular metal and nickel oxides, such as iron(III) or nickel(II), may be dissolved by the addition of a complexing acid, such as citric acid, and a reducing agent, such as oxalic acid.

Another phase, which may be performed between or during the individual steps described above and/or may conclude the treatment cycle, is a cleaning step, where any dissolved metal ions are typically removed from the coolant and accordingly from the cooling system e.g. by immobilization on an ion exchange resin.

WO 2011/134958 relates to a method for chemical decontamination of an oxide-coated surface, a cleaning cycle comprising one or more oxidation steps, followed by a decontamination step and an optional cleaning step. At least one oxidation step is carried out in an acid solution and at least one oxidation step is carried out in an alkaline solution.

WO 2016/124240 discloses a method for decontaminating metal surfaces in a cooling system of a nuclear reactor comprising at least one cycle, the cycle comprising an oxidation step, followed by a decontamination step, which is followed by a cleaning step. The oxidation step may be comprised of at least one acidic oxidation step and at least one alkaline oxidation step, or alternating acidic and alkaline oxidation steps.

WO 2018/134067 discloses a method for decontaminating metal surfaces of nuclear reactors, comprising an oxidation step, followed by a first cleaning step, followed by a decontamination step, which is followed by a second cleaning step.

Pick ME et al., Proceedings of the American Nuclear Society International Topical Meeting Waste Management and Decontamination and Decommissioning, September 14-18, 1986, Niagara Falls, Vol.2, pp 1399-141 is a review on methods for decontaminating metal surfaces in nuclear reactors and discloses a sequence of an alkaline oxidation with permanganate, followed by an acidic oxidation with permanganate, followed by a dissolution step.

One may distinguish between hard decontamination processes, which use more aggressive chemicals in a single step, such as cerium(IV), HNO_3/HF, or HBF_4 and soft decontamination processes, usually comprising several steps, such as the above-mentioned LOMI, CANDEREM, or CORD, which rely on the use of relatively mild organic acids as reducing agents at low concentrations.

Hard decontamination processes use more aggressive chemicals to increase the efficiency of the process. These processes penetrate into the base material, whereby the functionality of the material may be compromised. Commonly, hard decontamination processes are used during dismantling procedures.

The soft decontamination procedures are relevant for decontamination of cooling systems during plant operation and are able to remove contamination without damaging the cooling system surfaces.

Because of the mild character and low concentrations of the used chemicals in soft decontaminations, the efficiency of these processes is comparatively low and a so-called full system decontamination (FSD) require long treatment periods. Another disadvantage of chemical decontamination is the generation of relatively high volumes of secondary liquid waste.

The piping of a nuclear reactor is usually made of stainless steel or carbon steel. The steam generator tubes and main surfaces inside the primary circuit may include nickel alloys.

More specifically, the reactor pressure vessel and the piping of the primary circuit, which circulates the coolant that enters into direct contact with the reactor, is plated with austenitic stainless steel in all types of nuclear reactors.

The material of the steam generators, however, may vary. Steam generators are one of the key components of a nuclear power plant of the pressurized water reactor type. There, the heat released in the reactor and transported by the primary coolant is transferred to a secondary circuit, where steam is generated to power the turbines responsible for the operation of the electricity generation equipment. The heat transfer takes place through indirect contact of both liquids through the walls of hundreds to thousands of tubes within the steam generator. The heat-transfer surface of the steam generators is indeed so large, that it can represent approximately four fifths of the complete surface of the primary circuit.

In more homogeneous reactors, the steam generators consist of iron based alloys with varying amounts of other alloying elements.

In nuclear reactors of former Soviet design, steam generators often consist of austenitic stainless steel just like the plating of the rest of the primary circuit and the pressure vessel. In reactors of German design, the steam generators are generally made from Incoloy 800, an iron based alloy with comparable chromium content and higher nickel content than otherwise used austenitic stainless steels.

In American pressurized water reactors and the closely associated French, Japanese and Korean ones, the steam generators often consist of nickel based alloys with a high chromium content and a comparatively very lows percentage of iron, of either type Inconel alloy 600 in older designs, or Inconel alloy 690 in newer reactors.

The significant differences in the nature and composition of the base materials have a corresponding impact on the nature and characteristics of the oxides formed on the system surfaces during the nuclear power plant's operation.

These differences render the very fine tuned chemical processes for oxide dissolution that are effective on one reactor type often ineffective, at least locally where the oxides are different, on the other one.

It was for example previously described (Wood CJ, Prog Nucl Energy, 1900, 23(1), 35-80) that in contrast to boiling water reactors (BWR), and oxidation step is essential for pressure water reactor (PWR) decontamination. It was further stated, that alkaline oxidation yields higher decontamination factors (DF) when applied in the presence of high Ni alloyed materials, whereas acidic oxidation is preferred due to higher DFs in the presence of stainless steel surfaces.

Also according to Wood CJ, recent CAN-DECON and LOMI applications have each used alkaline permanganate (AP) followed by nitric acid/permanganate (NP) to achieve maximum chromium removal from oxide films initially present on both Inconel and stainless steel. The principle of pH switching was also described elsewhere (Smee JL et al., Recent Experience with Dilute Chemical Decontamination, Symposium On Advanced Nuclear Serviced – Proceedings, June 11, Canadian Nuclear Association, 1986, Toronto, Canada).

Although the principle of pH-switching to prepare oxides of different characteristics shows promise in principle, the reported application results would be considered only moderately successful by today's standards as found in Pick ME et al. already introduced above.

The inventors determined that the combination of conditions with the concentrations discussed above, does produce a comparatively large increase in the amount of radioactive waste generated by the decontamination chemicals for the relatively modest results obtained. This is the most obvious reason that the concepts disclosed above have not been developed further.

In the present field, it is common to differentiate the resulting waste from an application by origin, between so-called primary and secondary waste, which has been already mentioned above.

Primary waste is the one intrinsic to the system, i.e. corrosion products forming the contaminated oxide layer, and the radionuclides contained therein themselves. Their amount is given.

Secondary waste can be influenced by the choice of process. If higher concentrations of chemicals are used, secondary waste is higher. If lower concentrations prove to be just as effective, or methods can be used to reduce the waste volume generated by the chemicals employed, secondary waste is lower.

This differentiation serves enables a comparison between various processes, to determine which is more advantageous. All resulting waste, both primary and secondary, is obtained mixed, and has to be disposed of as radioactive waste. This is associated with efforts and costs considerably higher than those of conventional, nonradioactive industrial waste.

A complete separation between them, or between radioactive and nonradioactive matter, is not possible in practice without considerable additional efforts. Reducing the amount of secondary waste at input is considerably easier, and a process comprising a lower amount of secondary waste generation for the same effectivity, considered preferable in most cases.

The procedures as described in Wood CJ, Pick ME et al., and Smee Jl et al., generated waste in a proportion of approximately 20% primary waste to 80% secondary waste. These procedures, while recognizing that different surfaces need different treatments, where never developed further in order to make it applicable at a FSD scale, and even at the component scale it was later, as far as published results are concerned, abandoned.

Accordingly, while the previously mentioned processes have established a largely effective and efficient methodology for the FSD scale treatment of nuclear power reactors with relatively homogeneous materials, one such methodology is not yet established for nuclear power reactors with marked differences in the characteristics of the construction materials, and of the oxides formed thereon.

It is thus a technical problem of the present invention to provide a decontamination process suitable for various surfaces of a cooling system of a nuclear power plant.

It is a further technical problem of the present invention to provide a decontamination process, which generates a reduced amount of secondary waste.

It is also a technical problem of the present invention to provide a decontamination process which is completed in a short period of time.

Summary of the Invention

The present invention thus relates to method of decontaminating metal surfaces in a cooling system of a nuclear reactor, wherein the metal surfaces are coated with a solid metal oxide layer including radionuclides, the method comprising at least one treatment cycle, wherein the treatment cycle comprises:

a) at least two subsequent oxidation steps, wherein one oxidation step comprises:
   a1) contacting the solid metal oxide layer including radionuclides with an aqueous solution comprising a permanganate oxidant,
   a2) contacting unreacted permanganate oxidant, if present, and insoluble manganese compounds obtained in step a1) with an aqueous solution of a reducing agent,
   a3) removing solubilized metal oxides and released radionuclides, including solubilized manganese compounds obtained in steps a1) and a2),
b) a dissolution step, wherein the solid metal oxide layer including radionuclides of step a) is further contacted with an aqueous solution of an organic acid, and
c) a cleaning step, wherein solubilized metal oxides and released radionuclides of step b) are removed.

Preferably, for each the at least two subsequent oxidation steps of a), the permanganate oxidizing agent in step a1) is individually selected from an acidic permanganate oxidant and an alkaline permanganate oxidant.

Preferably, in at least one of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an acidic permanganate oxidant, and in at least one of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an alkaline permanganate oxidant.

It is also preferred that in the first of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an acidic permanganate oxidant.

It is further preferred that in the first two, more preferably the first three, even more preferably the first four, of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an acidic permanganate oxidant.

It is preferred that in the last of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an alkaline permanganate oxidant.

It is further preferred that in the last two, more preferably the last three, even more preferably in the last four, of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an alkaline permanganate oxidant.

Preferably, the acidic permanganate oxidant acidic permanganate oxidant of step a1) is selected from the group consisting of $HMnO_4$, $HMnO_4/HNO_3$, $KMnO_4/HNO_3$, $HMnO_4/H_3PO_4$, $KMnO_4/H_3PO_4$, $KMnO_4$/methane sulfonic acids, $HMnO_4$/methane sulfonic acids, and/or combinations thereof.

Preferably, the alkaline permanganate oxidant is selected from $KMnO_4$/LiOH, $KMnO_4$/NaOH, $KMnO_4$/KOH, and/or combinations thereof.

Preferably, the aqueous solution of the acidic permanganate oxidant has a pH value of less than 6, preferably less than 4.

Preferably, the aqueous solution of the alkaline permanganate oxidant has a pH value of at least 8, preferably at least 10.

Preferably, the reducing agent of step a2) is selected from the group consisting of oxalic acid, formic acid, glyoxylic acid, citric acid, picolinic acid, ascorbic acid, ethylenediamine-tetraacetic acid, methylsulfonic acid, nitrilotriacetic acid, hydrogen peroxide, hydrazine, hydrogen and/or combinations thereof.

Preferably, step a2) and a3) are performed at least in parts simultaneously, more preferably step a2) and a3) are performed entirely simultaneously.

It is further preferred that the organic acid of step b) is selected from the group consisting of oxalic acid, formic acid, glyoxylic acid, citric acid, picolinic acid, ascorbic acid,

ethylenediamine-tetraacetic acid, methylsulfonic acid, nitrilotriacetic acid, and/or combinations thereof.

Optionally, the present method further comprises d) a decomposition step.

Detailed Description of the Invention

The present invention thus relates to method of decontaminating metal surfaces in a cooling system of a nuclear reactor, wherein the metal surfaces are coated with a solid metal oxide layer including radionuclides, the method comprising at least one treatment cycle, wherein the treatment cycle comprises:

a) at least two subsequent oxidation steps, wherein one oxidation step comprises:
   a1) contacting the solid metal oxide layer including radionuclides with an aqueous solution comprising a permanganate oxidant,
   a2) contacting unreacted permanganate oxidant, if present, and insoluble manganese compounds obtained in step a1) with an aqueous solution of a reducing agent,
   a3) removing solubilized metal oxides and released radionuclides, including solubilized manganese compounds obtained in steps a1) and a2),
b) a dissolution step, wherein the solid metal oxide layer including radionuclides of step a) is further contacted with an aqueous solution of an organic acid, and
c) a cleaning step, wherein solubilized metal oxides and released radionuclides of step b) are removed.

According to the method of the present invention, a metal oxide layer containing radioisotopes is effectively removed from metal surfaces of a nuclear facility, and in particular from metal surfaces located in the primary cooling system of a nuclear reactor. The primary cooling system is understood as comprising all systems and components which are in contact with the primary coolant during reactor operation, including but not limited to the reactor vessel, reactor coolant pumps, pipework and steam generators, as well as auxiliary systems such as the volume control system, pressure reducing station and reactor water clean-up system.

The decontamination method of the present invention is particularly useful for decontamination of the primary cooling system or components thereof in a boiling water reactor or a pressurized water reactor, and preferably a nuclear reactor comprising steam

generator piping having metal surfaces of nickel alloys such as Inconel™ 600, Inconel™ 690 or Incoloy™ 800, and/or materials with a high chromium content, or large surfaces of chromium containing materials.

Even more preferably, the method of the present invention is particularly useful for the decontamination of the primary cooling system or components thereof in a nuclear reactor comprising a combination of various metal surfaces of nickel alloys such as Inconel™ 600, Inconel™ 690 or Incoloy™ 800, and materials with a high chromium content.

According to the present invention, one oxidation step is not immediately followed by one dissolution step. Instead, at least two subsequent treatment steps are performed before a dissolution step is performed. Thus, one oxidation step of the present invention is defined to comprise three sub-steps a1), a2), and a3). At least two such oxidation steps are performed subsequently.

None of the methods of the prior art as mentioned herein further comprise present sub-steps a2) and a3) between oxidation steps of contacting a solid metal oxide layer including radionuclides with a permanganate oxidant as known in the prior art and consequently the specific combination of the three present steps a1), a2), and a3), which are performed at least twice in a row. **Figure 1** schematically shows the processes occurring on the treated metal surfaces during a treatment cycle according to the prior art, such as WO 2011/134958, compared with the processes taking place during treatment cycle according an embodiment of the present invention, where a2) and a3) are performed simultaneously.

Methods according to the publications by Pick and Wood, and those described in WO 2011/134958 and the like share a common technical difficulty when applying subsequent oxidations during the same treatment cycle, which is the accumulation of permanganate decomposition products on the surfaces. This effectively impedes at some point the mass exchange between surface and solution, rendering further oxidation phases ineffective. Additional oxidation phases beyond this point have to further effect and result in an unnecessary and ineffective consumption of time and generation of waste.

This problem is solved by the present invention by further introducing sub-steps a2) and a3) between oxidation phases as known in the prior art, said oxidation phases comprising contacting a solid metal oxide layer contaminated with radionuclides with a permanganate oxidant. These sub-steps effectively remove permanganate decomposition products, i.e.

insoluble manganese compounds, from surface, thus enabling fresh oxidation solution to access the oxide surface to be treated without any diffusion problems.

In **Figure 1**, during the treatment cycle according to WO 2011/134958 (upper panel), permanganate decomposition products or insoluble manganese compounds (IMC), such as hydrated Mn(IV)-oxide and Mn(II)-hydroxide, are formed during oxidation, and accumulate on the surface during the plurality of oxidation steps, preventing at one point the permanganate oxidant (PO) to access the affected oxide (AO) and unaffected oxide (UO).

UO is oxide in its original state. Under e.g. pressurized water reactor water chemistry conditions, UO consists mainly of chromium-nickel-ferrites as mentioned earlier in the introduction, which are insoluble in e.g. oxalic acid or other comparatively mild organic acids, and require a pretreatment with permanganate or another oxidant in order to be easier to solubilize. AO is an oxide depleted in chromium and nickel that has been affected by the oxidative pretreatment with permanganate, and can now be readily solubilized by e.g. oxalic acid or other comparatively mild organic acids.

During a treatment cycle of the present invention as shown in **Figure 1** (lower panel), favourably, the IMC are removed from the surface during steps a2) and a3), thus preventing their accumulation on the affected oxide (AO) and enabling permanganate oxidant (PO) contact, resulting overall in a cleaning process finalized in a shorter time and generating less waste.

The insoluble manganese compounds removed during steps a2) and a3) are labeled removed insoluble manganese compounds (RIMC) to distinguish them from the dissolved oxide components (DOC) from previous step a1). DOC comprise essentially chromium and nickel oxides, RIMC comprise mainly manganese oxides.

These improvements are favourably suitable, in particular for large-scale technical applications, since the performance of several subsequent oxidation steps enables the near complete leaching out of chromium and nickel of the oxide surfaces, leaving iron and activity on the surfaces in expectation of the oxide dissolution phase. Through this, different oxide characteristics, and different oxide solubilities are evened out.

Thus, the danger of large-scale particle generation is avoided. Particle release is a known consequence of dissolution of oxides with different characteristics, when the oxides with

better solubility are dissolved, the ones remaining that grew on those, or are exposed to high flow where they were previously shielded by the now absent oxides, are released as solids. Since these oxides contain radioactive matter as well, their release into the circuit is problematic. Consequences can range from their accumulation is areas of complicated geometry or low flow resulting in so called hot-spots, to the clogging of filters or detrimental effects of moving components.

According to the present invention, only after the effect of the combination of oxidative treatments has been exhausted, chromium and nickel have been leeched out and the remaining oxides are as far as feasible homogeneous, does the process then proceed to the dissolution phase.

The decontamination treatment can be carried out on reactor subsystems and components. Preferably, the decontamination method of the present invention is carried out as full system decontamination. During full system decontamination the contaminated metal oxide layer is removed from all metal surfaces in the reactor cooling system that are in contact with the primary coolant during reactor operation. Typically, full system decontamination involves all parts of the primary coolant circuit and the steam generator as well as the volume control system, the pressure reducing station and possibly other systems which are contaminated to a certain extent.

Preferably, the decontamination method can be applied using an external decontamination equipment for injection of decontamination chemicals, for monitoring the decontamination treatment, for increasing the available ion exchange rate, and for achieving the decontamination targets in a faster, more economical and safer way. The process temperatures are preferably kept below the boiling point of water at atmospheric pressure in order to eliminate the need of using complex and expensive pressure-proof components for the external decontamination equipment.

The chemicals used for the decontamination treatment can be injected into the primary coolant circuit of the nuclear reactor at a dosing station located in the low-pressure part of the coolant circuit. Preferably, the external decontamination equipment is used for dosing the decontamination chemicals.

Chemicals and other materials such as ion exchange materials used in the decontamination method of the present invention are commercially available and can be held in stock at the nuclear power plant facilities.

In general, more than one decontamination treatment cycles are carried out in order to achieve a satisfactory reduction of activity on the metal surfaces. The reduction of surface activity and/or the dose reduction correlating to surface activity reduction is referred to as "decontamination factor". The decontamination factor is calculated either by the specific surface activity before decontamination treatment divided by the specific surface activity after the decontamination treatment, or by the dose rate before decontamination treatment divided by the dose rate after decontamination treatment.

Preferably, the decontamination factor of a technically satisfying decontamination treatment is greater than 10.

The various steps of the decontamination method of the present invention are now described in greater detail below.

Step a) – Oxidation Step

Step a) of the method of the present invention comprises at least two subsequent oxidation steps, wherein one oxidation step comprises sub-steps a1), a2), and a3), comprising a1) contacting the solid metal oxide layer including radionuclides with an aqueous solution comprising a permanganate oxidant, a2) contacting unreacted permanganate oxidant, if present, and insoluble manganese compounds obtained in step a1) with an aqueous solution of a reducing agent, a3) removing solubilized metal oxides and released radionuclides, including solubilized manganese compounds obtained in steps a1) and a2).

According to the method of the present invention, at least 2 subsequent oxidation steps a) are performed. More preferably at least 3, even more preferably at least 4, even more preferably at least 5, most preferably at least 6 subsequent oxidation steps a) are performed.

It is further preferred that 2 to 20, more preferably 2 to 15, more preferably 2 to 10, even more preferably 2 to 5 subsequent oxidation steps a) are performed.

The amount of oxides to be removed and their characteristics tend to vary even within very similar plants due to their operating history and the precise parameters of the water chemistry applied. The number and nature of the oxidation steps can be further determined more precisely either experimentally on the base of representative artefacts of plant material, based on operational experience, and the evaluation of data acquired during the application.

Step a1) – Contacting metal surface with permanganate oxidant

Step a1) comprises contacting the solid metal oxide layer including radionuclides with an aqueous solution comprising a permanganate oxidant. Thereby, at least part of insoluble metal oxides of the solid metal oxide layer are converted into soluble metal oxides, whereby at least part of the radionuclides are released from the solid metal oxide layer and insoluble manganese compounds are formed.

The conversion of at least part of insoluble metal oxides of the solid metal oxide layer into soluble metal oxides is achieved by increasing the oxidation state of at least part of insoluble metal oxides. In particular, Cr(III) in the metal oxide layer is oxidized to form soluble Cr(VI) compounds, and the Cr(VI) compounds are dissolved in the permanganate-based oxidation solution. Depending on the pH value of the oxidation solution, the Cr(VI) compound may comprise chromic acid, dichromic acid and/or salts thereof.

As a by-product insoluble manganese compounds such hydrated Mn(IV)-oxide and Mn(II)-hydroxide are formed. These solid manganese compounds may circulate in the aqueous solution but are generally deposited on the metal surfaces of the cooling system.

Preferably, in at least one of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an acidic permanganate oxidant, and in at least one of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is and an alkaline permanganate oxidant.

It is further preferred that in the first of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an acidic permanganate oxidant.

It is even more preferred that the first two, more preferably the first three, of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an acidic permanganate oxidant.

It is preferred that in the last of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an alkaline permanganate oxidant.

Preferably, the acidic permanganate oxidant acidic permanganate oxidant of step a1) is selected from the group consisting of $HMnO_4$, $HMnO_4/HNO_3$, $KMnO_4/HNO_3$, $HMnO_4/H_3PO_4$, $KMnO_4/H_3PO_4$, $KMnO_4$/methane sulfonic acids, $HMnO_4$/methane sulfonic acids, and/or combinations thereof. Preferably, the acidic permanganate oxidant is $HMnO_4$.

Preferably, the aqueous solution of the acidic permanganate oxidant has a pH value of less than 6, preferably less than 4.

Preferably, the pH of the oxidation solution is maintained at or above 2.5, which can be achieved using permanganic acid as the sole oxidant. Carrying out of the oxidation step at a pH > 2.5 can avoid substantial corrosion of the metal surface to be decontaminated. In addition, the absence of an additional mineral acid in the oxidation solution avoids too high dissolution rates of the metal oxide layer which could be detrimental in FSD operations.

Preferably the aqueous solution of the acidic permanganate oxidant has a pH value in the range of 2.5 to 6, preferably in the range of 2.5 to 4.

Preferably, the alkaline permanganate oxidant is selected from $KMnO_4$/LiOH, $KMnO_4$/NaOH, $KMnO_4$/KOH, and/or combinations thereof.

Preferably, the aqueous solution of the alkaline permanganate oxidant has a pH value of at least 8, preferably at least 10. Preferably the aqueous solution of the alkaline permanganate oxidant has a pH value in the range of 8 to 13, more preferably 10 to 12.

Permanganic acid is preferred over alkali metal permanganate salts because less waste is produced.

Preferably, the concentration of the permanganate oxidant in the oxidation solution within the primary cooling system is controlled to be in the range of from 10 to 800 mg/kg during the oxidation step, and preferably to range from 50 to 300 mg/kg.

If the concentration of the permanganate oxidant in the oxidation solution is lower than 10 mg/kg, the reaction rate of the oxidation may be too low and several additional injections may be required. If the concentration of the permanganate oxidant in the oxidant solution exceeds 800 mg/kg, a large excess of the oxidant may be present at the end of the oxidation step which can generate an unnecessary amount of waste.

Preferably, the amount of the permanganate oxidant is controlled to be as low as possible at the end of the oxidation step because removal of excess permanganate oxidant will increase the amount of secondary waste.

Step a1) is faster at higher temperatures. Accordingly, higher oxidation temperatures are preferred. Preferably, the oxidation step is carried out at a temperature of between about 20 to 150°C, more preferably at a temperature of from 90 to 125°C. However, it is also possible to carry out step a1) at temperatures of up to 120°C at a higher than atmospheric pressure, with or without the use of an external decontamination device. Step a1) is preferably performed for a period of time in the range of 2 to 48 h.

Preferably, the progress of the oxidation step is monitored by controlling the amount of the permanganate oxidant remaining in the oxidation solution, and by monitoring the concentration of Cr(VI) dissolved in the permanganate-based oxidation solution. As long as the oxidation reaction continues and the oxidation of the metal oxide layer is incomplete, the permanganate oxidant continues to be consumed and, in most cases, the concentration of Cr(VI) compounds increases. Step a1) is terminated as soon as no further increase of Cr(IV) concentration is determined.

The amount of permanganate and Cr(VI) in solution by be determined by photometric measurements, by determining the ORP, and/or by determining a concentration of through an instrumental analysis technique such as atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP) mass spectrometry.

The residence time of the oxidation solution in the cooling system during the oxidation step may comprise a plurality of hours, preferably 30 hours or more in large and complex

applications such as full system decontaminations. It is desired that the oxidation of the metal oxide layer is substantially complete so that as much as possible of the metal oxide layer thickness is reacted during the oxidation step.

Preferably, the oxidation step is terminated when no further increase of the Cr(VI) concentration in the oxidation solution can be determined, more preferably when the permanganate concentration in the oxidation solution has stabilized additionally at an essentially constant concentration level and permanganate oxidant is no longer being consumed, and most preferably when the permanganate oxidant has been completely consumed.

Instead of, or in addition to, monitoring the concentration of Cr(VI) and/or permanganate, it is also possible to monitor the presence of the radioisotope Cr-51 in the oxidation solution by means of gamma spectroscopy.

For carrying out the oxidation step, an aqueous solution of the permanganate oxidant is suitably injected into the primary coolant within the primary coolant circuit or the subsystem which is to be decontaminated, and the aqueous oxidation solution comprising the permanganate oxidant is circulated through the system. Preferably, the permanganate oxidant is injected into a low-pressure section of the cooling and/or moderator system.

Examples for suitable injection positions are the volume control system, the reactor water clean-up system and/or a residual heat removal system. More preferably, the solution of the permanganate oxidant can be introduced into the primary cooling system or moderator system by means of an external decontamination device.

Step a2) - Contacting unreacted permanganate and insoluble manganese compounds with reducing agent

Step a2) comprises contacting unreacted permanganate oxidant, if present, and insoluble manganese compounds obtained in step a1) with an aqueous solution of a reducing agent.

Thereby, any unreacted permanganate oxidant is converted into soluble Mn(II)-compounds and insoluble Mn(IV)-compounds are also converted into soluble Mn(II)-compounds. The aqueous solution of the reducing agent is further suitable to dissolve Mn(II)-hydroxides.

In order to maximize effectiveness of each individual oxide preparation treatment, a complete removal of the decomposition products of the permanganate from the treated surfaces is key. Through this, complete access of the new oxidation solution to the oxide surface is enabled, without the diffusion problems that would have hindered it in the past.

Removal of the permanganate oxidant and insoluble manganese compounds is effected by reacting permanganate with a stoichiometric or under-stoichiometric amount of a reducing agent without changing the oxidation state of the Cr(VI) compound.

Preferably, the reducing agent of step a2) is selected from the group consisting of hydrogen, hydrogen peroxide, hydrazine, inorganic acids, non-chelating monocarboxylic acids, non-chelating dicarboxylic acids, and derivatives thereof.

The reducing agent preferably is an inorganic or an organic acid. More preferably, the reducing agent of step a2) is selected from the group consisting of nitriloacetic acid, oxalic acid, formic acid, glyoxylic acid, citric acid, picolinic acid, ascorbic acid, ethylenediaminetetraacetic acid, methylsulfonic acid, nitrilotriacetic acid, hydrogen peroxide, hydrazine, hydrogen and/or combinations thereof. Preferably, the reducing agent is oxalic acid.

Suitable concentrations of the reducing agent are generally between 50 mg/kg and 10000 mg/kg, and preferably 100 mg/kg to 5000 mg/kg. The concentrations will depend on the reducing agent used. Step a2) is preferably performed at temperatures of 50 to 95°C. Step a2) is preferably performed for a period of time of 12 to 72 h.

Step a2) is monitored by determining the amount of residual permanganate preferably via titration or photometric measurements, and/or electrochemical measurements that reflect the permanganate concentration, such as conductivity, ORP (oxidation reduction potential) or pH. Preferably, step a2) is completed when the above measurements indicate the absence of permanganate.

For carrying out step a2), the introduction of permanganate may be stopped and an aqueous solution of one or more reducing agents may be injected into the primary coolant within the primary coolant circuit or the subsystem which is to be decontaminated. Suitably, the reducing agent is injected so that no surplus is generated in solution.

Step a3) – Removal of solubilized metal oxides

Step a3) comprises removing solubilized metal oxides and released radionuclides, including solubilized manganese compounds, obtained in steps a1) and a2).

Suitable methods for the removal of solubilized metal oxides and released radionuclides, including solubilized manganese compounds may be selected from suitable waste water treatment methods such as electrodeposition, membrane separation, osmosis, ultrafiltration, drain and rinse with posterior treatment of resulting effluents in an evaporator, and/or immobilization on an ion exchange resin. Preferably, the methods for the removal of solubilized metal oxides and released radionuclides, including solubilized manganese compounds is selected from drain and rinse with posterior treatment of resulting effluents in an evaporator and/or immobilization on an ion exchange resin.

More preferably, the solubilized metal oxides and released radionuclides, including solubilized manganese compounds are removed by and immobilization on an ion exchange resin.

Suitable ion exchange materials for use in removal step a3) are resistant to the harsh oxidizing and optionally acidic conditions present in the oxidation solution. It is also possible to use different ion exchange materials or combinations of ion exchange materials each being optimized for the specific conditions in the different process.

Ion exchange materials suitable for use in the decontamination method of the present invention are commercially available, such as ion exchange resins from producers such as Lewatite™ from Lanxess, Diaion from Mitsubishi Chemicals or from Purolite. Further preferred are nuclear grade ion exchange resins. The ion exchange materials can be included in the external decontamination device, and may be configured as membranes or ion exchange columns filled with the ion exchange material. Alternatively or additionally, the inventors contemplate use of the ion exchange materials which are present in the reactor water clean-up system or any other suitable internal system of the nuclear facility.

Preferably, the ion exchange material is contained within an external module which is preferably configured for a prompt charge and discharge of different amounts of said material. More preferably, the external module is an integral part of the external decontamination equipment.

The ion exchange material may be an ion exchange resin. Preferably, the ion exchange material is an ion exchange resin which is employed during power generating operation of the nuclear facility.

Preferably, the ion exchange material is an inorganic ion exchange material. Use of an inorganic ion exchange material is advantageous in that it is resistant to harsh oxidizing conditions and chemically stable over long disposal times.

Steps a2) and a3) may be performed subsequently. Thus, the removal according to step a3) is started when step a2) is terminated, that is when no further increase of the Cr(VI), Mn(II), and radioisotope concentration in the aqueous solution can be determined.

Preferably, steps a2) and a3) may be performed at least in parts simultaneously. Preferably, the aqueous oxidation solution containing soluble Cr(VI) ions, Mn(II) ions and radioisotopes is passed over the ion exchange material preferably before the chromium concentration has stabilized in the oxidation solution, i.e. while the chromium concentration is still increasing. This can be used to achieve time savings.

More preferably, steps a2) and a3) are performed entirely simultaneously. Thereby, additional time may be saved.

The ion exchange material preferably is either discarded directly after its use, or any process solution containing organic acid is prevented from flowing through the ion exchange material used in the first cleaning step by appropriate valve positioning in the decontamination circuit, so that use of the ion exchange material can be resumed in a posterior treatment cycle if its capacity has not yet been exhausted.

Further, preventing the ion exchange material from being exposed to the organic acid facilitates and/or enables the use of inorganic ion exchange materials. These materials are suitable for the first cleaning step of the present invention, but have not been employed for any reported chemical decontamination application due to their general incompatibility with organic acids used in the dissolution step.

Step a3) is controlled by monitoring the removal of the Cr(VI) ions, Mn(II) ions and radioisotopes from the aqueous solution, preferably by photometric measurements, by determining the ORP, and/or by determining a concentration of chromium and manganese

through an instrumental analysis technique such as atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP) mass spectrometry.

As soon as the removal of the Cr(VI) and Mn(II) ions and radioisotopes is completed or the concentration of the Cr(VI) and Mn(II) ions and radioisotopes is below a predetermined target value, the dissolution step b) further described below is started.

For carrying out step a3), the introduction of the reducing agent for a2) may stopped and the aqueous solution is treated by one of the aforementioned methods, e.g. passed over an ion exchange resin. As disclosed above, steps a2) and a3) may be performed in parts simultaneously or entirely simultaneously.

Step b) – Dissolution

The method of the present invention further comprises b) a dissolution step, wherein the solid metal oxide layer including radionuclides of step a) is further contacted with an aqueous solution of an organic acid.

Thereby, at least part of metal oxides, which are soluble in the organic acid, of the solid metal oxide layer, and thereby at least part of the radionuclides from the solid metal oxide layer is released.

In the dissolution step, the metal oxide layer subjected to the oxidation step is contacted with an aqueous solution of an organic acid. The organic acid serves as a dissolution reagent and dissolves the metal oxides, in particular Fe(III) ions and radioactive matter incorporated in the metal oxide layer, thereby forming an aqueous solution containing the organic acid, one or more metal ions dissolved from the metal oxide layer, and the radioactive matter.

Preferably, the organic acid used in dissolution step b) is a monocarboxylic acid. Preferably the organic acid used in dissolution step b) is selected from the group consisting of formic acid and glyoxylic acid, aliphatic dicarboxylic acids such as oxalic acid, alkali metal salts of monocarboxylic acids and aliphatic dicarboxylic acids, and mixtures thereof.

Preferably, the organic acid of step b) is selected from the group consisting of oxalic acid, formic acid, glyoxylic acid, citric acid, picolinic acid, ascorbic acid, ethylenediamine-

tetraacetic acid, methylsulfonic acid, nitrilotriacetic acid, and/or combinations thereof. Most preferably, the organic acid is oxalic acid.

Preferred concentrations of the acid in step b) are 50 mg to 10000 mg/kg, more preferably 100 mg/kg to 5000 mg/kg. Step b) is preferably performed at temperatures of 50 to 125°C, and more preferably from 60 to 99°C. Preferably step b) is performed for a period of time of 2 to 120 h, more preferably 2 to 48 h.

The progress of the dissolution step can be monitored by measuring the concentration of selected radioisotopes and metal ions. Samples can be taken from the dissolution solution and analyzed by spectroscopic methods such as atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) mass spectrometry. The amount of radioisotopes dissolved in the dissolution solution can be determined by different methods of gamma spectroscopy, such as by means of high purity germanium detectors, sodium iodide detectors, or by other suitable methods depending on the nature of the radioisotopes present.

The dissolution step is terminated as soon as no substantial increase of the amount of metal ions removed from the dissolution solution is determined, and/or no further increase of the activity of the radioisotopes can be measured.

For carrying out step b), the removal, e.g. the passing over the ion exchange resin, may be stopped or continue in operation, and an aqueous solution of the organic acid is injected into the primary coolant within the primary coolant circuit or the subsystem which is to be decontaminated.

Step c) - Cleaning

The present method further comprises c) a cleaning step, wherein solubilized metal oxides and released radionuclides of step b) are removed.

Similar to step a3), suitable methods for the removal of solubilized metal oxides and released radionuclides may be selected from suitable waste water treatment methods such as electrodeposition, membrane separation, osmosis, ultrafiltration, drain and rinse with posterior treatment of resulting effluents in an evaporator and/or immobilization on an ion exchange resin. More preferably, the methods for the removal of solubilized metal oxides

and released radionuclides is selected from drain and rinse with posterior treatment of resulting effluents in an evaporator and/or immobilization on an ion exchange resin

Suitable methods for the removal of solubilized metal oxides and released radionuclides may be selected from suitable waste water treatment methods such as electrodeposition, membrane separation, osmosis, ultrafiltration, drain and rinse with posterior treatment of resulting effluents in an evaporator and/or immobilization on an ion exchange resin. More preferably, the methods for the removal of solubilized metal oxides and released radionuclides is selected from drain and rinse with posterior treatment of resulting effluents in an evaporator and/or immobilization on an ion exchange resin

More preferably, the solubilized metal oxides and released radionuclides are removed by and immobilization on an ion exchange resin.

With regard to the immobilization on an ion exchange resin it is further referred to the disclosure for step a3).

During step c), all ions dissolved in the dissolution solution are removed from the dissolution solution and are permanently captured on the ion exchange material.

The cation exchange material may be a ion exchange resin of the type employed in the nuclear power plant during power generating operation, or any other suitable ion exchange material. Preferably, the ion exchange material used in the dissolution step is a ion exchange resin which is present in the water clean-up system of the nuclear reactor.

The organic acid dissolved in the dissolution solution may be regenerated by release of hydrogen ions during the cation exchange reaction. Therefore, the organic acid is not depleted in the dissolution step, and can be used continuously for dissolution of the metal oxide layer. Accordingly, it is possible to employing sub-stoichiometric amounts of the organic acid.

The decontamination of the metal surface covered with the metal oxide layer is only limited by a decrease of the solubility of the metal oxide layer which is due to the fact that the metal oxide layer reacted in the oxidation step is completely removed at the end of the dissolution step. Therefore, a further oxidation of the remaining metal oxide layer is often required to dissolve additional metal ions from the metal oxide layer into the dissolution solution.

Similar, the progress of the ion exchange can be monitored by measuring the concentration of selected radioisotopes and metal ions. Samples can be taken from the dissolution solution and analyzed by spectroscopic methods such as atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) mass spectrometry. The amount of radioisotopes dissolved in the dissolution solution can be determined by different methods of gamma spectroscopy, such as by means of high purity germanium detectors, sodium iodide detectors, or by other suitable methods depending on the nature of the radioisotopes present.

The removal is terminated as soon as no substantial increase of the amount of metal ions removed from the dissolution solution is determined, and/or no further increase of the activity of the radioisotopes can be measured.

For carrying out step a3), the introduction of the organic acid is injected according to step a3) maystopped and the aqueous solution is treated by one of the aforementioned methods, e.g. passed over an ion exchange resin.

Step d) – Inactivation

Optionally, the method of the present invention further comprises a step d) of inactivation of the organic acid used in step b).

Before starting a further oxidation step to solubilize the metal oxide layer now exposed by the dissolution solution, the organic acid may be removed from the dissolution solution.

For example, the system can be drained and rinsed with additional water until the organic acid is completely removed. However, this is the least favoured option, because it would generate a large amount of radioactive liquid waste. The water would have to be treated at a later stage in such a way that no chelates are generated.

The organic acid can also be removed by ion exchange mechanisms, but this would generate undesired chelate-containing waste.

According to another option, the organic acid can be removed from the dissolution solution by reacting the organic acid with permanganic acid or another permanganate or oxidizing

compound. The process of decomposing the organic acid by reacting with permanganate can preferably be used for decontamination systems having small volumes, e.g. during the decontamination of isolated heat exchangers and the like. However, this reaction requires a substantial amount of permanganic acid or other permanganate compound and also generates additional secondary waste in the form of e.g. manganese ions that have to be removed from the solution via ion exchange, in a way comparable to the other metal cations generated from the metal oxide layer.

Therefore, the decontamination method may further a decomposition step using another method for the reduction of the organic acid present in the dissolution solution, such as photocatalytical oxidation of the organic acid.

An oxidation of the organic acid itself, photocatalytically or otherwise, does not necessarily generate additional radioactive waste since the decomposition of the organic matter results in the formation of water and carbon dioxide. Therefore, selecting an appropriate decomposition method makes it possible to avoid the formation of any unnecessary secondary radioactive waste in this stage.

Preferably, the organic acid is reacted with an oxidant that does not contribute to the amount of radioactive waste generated during the decontamination process. Preferably, the organic acid is decomposed to form carbon dioxide and water. More preferably, the organic acid is decomposed by reacting the organic acid with an oxidant such as hydrogen peroxide, most preferably while simultaneously exposing the dissolution solution to UV radiation.

Use of hydrogen peroxide is advantageous because it is an industrial chemical which is commercially available and can be stored in stock solutions at the nuclear plant facilities. Oxygen or ozone could also be used for decomposing the organic acid, but are less preferred because these oxidants require additional equipment and are associated with other risks, especially in the case of ozone. Preferably, a photocatalytical oxidation is employed to increase the reaction speed.

Preferably, the temperature of the dissolution solution during decomposition of the organic acid is maintained between 20 and 95°C.

A UV reactor is preferably immersed into the dissolution solution to maximize the area of exposure to UV light, and hydrogen peroxide is injected into the dissolution solution

upstream of the UV reactor such that the hydrogen peroxide is thoroughly mixed with the dissolution solution prior to reaching the UV reactor.

The injection of hydrogen peroxide into the dissolution solution is preferably controlled so that no hydrogen peroxide is determined downstream of the UV reactor.

Preferably, hydrogen peroxide downstream of the UV reactor is monitored continuously, and the rate of the hydrogen peroxide injection is adjusted accordingly.

The decomposition of the organic acid is preferably terminated if the dissolution solution is completely depleted of the organic acid, including the organic acid bound in chelate complexes. While less preferred, but also possible depending on project objectives and local specific considerations, the dissolution solution can be depleted to a concentration of the free organic acid in the solution of up to 50 mg/kg or less. Higher concentrations of free organic acid are also possible but even less preferable, due to an increase of permanganate consumption in a subsequent treatment cycle.

In a final cleaning step, when the metal oxide layer is completely removed from the metal surface and/or the desired decontamination factor is achieved, the conductivity of the primary coolant may be controlled to be 10 µS/cm at 25°C or lower, although final water quality criteria can vary from facility to facility. Preferably, the final cleaning step is conducted at a temperature of 70°C or less, more preferably 60°C or less.

The inactivation step d) may already be started during the decontamination step b). The dissolution solution may then be passed over an ion exchange resin while the organic acid is simultaneously decomposed, for instance by photocatalytic oxidation.

Figures

Figure 1 shows processes occurring on the treated metal surfaces during a treatment cycle according to the prior art, such as WO 2011/134958 (upper panel), compared with the processes occurring during a treatment cycle according to the present invention (lower panel).

Figure 2 shows a basic chemical decontamination circuit.

Figure 3 shows graph illustrating the evolution of the concentration of metallic elements in solution during an alternation of chemical decontamination cycles between acidic and alkaline conditions, as per the provided literature describing the prior art, such as Pick ME et al. and Smee JL et al.

Figure 4 shows a graph illustrating the evolution of the concentration of metallic elements in solution during an application according to the current state of the art for pH-switching during a chemical decontamination cycle.

Figure 5 shows a graph illustrating the evolution of the concentration of metallic elements in solution during an application of chemical decontamination cycle according to the present invention.

Experimental

The methods claimed in the invention can be reproduced by repetition of the experiments described henceforth. For their performance, the use of a circuit according to the schematic representation in **Figure 2** is particularly convenient.

The materials of the circuit are inert in nature under the conditions of the experiments, so that no input material from them influences the measurements performed. Chemically and temperature resistant glass is particularly suitable for this purpose, but the use of other materials such as PTFE or similar polymers, or combinations thereof, is also conceivable.

The circuit consists of a main tank containing the main volume of the circuit, equipped with a heater, and connected to a supply of demineralized water, and a draining system suitable for acceptance of effluents containing chemicals. A chemical injection system is attached to the tank. The tank is equipped with several sample holder racks, which are manufactured from an inert material as well. The tank is connected to a circulation pump. The pump draws liquid from the tank and transports it through piping to a column design for holding ion exchanger beads.

The resin column has two different sampling points, one upstream of the column (before resin) and one downstream of the column (after resin). A method of online or inline sampling is preferred, but in principle, intermittent liquid sampling via e.g. liquid sample bottles can

be suitable as well. The most preferred method for liquid chemical analysis due to its ease of automatization, use, and precision, is ICP.

Other suitable methods for liquid chemical analysis such as e.g. AAS, photometry, etc. can be used in its stead as well. After passing through the ion exchange column, the liquid is discharged back to the tank. A flow indicator is installed in the piping. A mass balance of the amount of analytes before the resin and the amount of analytes after the resin is used to evaluate total amounts removed from solution via ion exchange, and current load of the resins.

The sample racks in the tank are loaded with several samples of different materials that have been exposed to simulated nuclear power plant primary circuit conditions to generate oxide layers comparable in nature to those present in a nuclear power plant, without inclusion of radionuclides. Actual real radioactive material can be treated as well where available and under the necessary organizational and other conditions.

A proportion between the surface of Inconel 600 or Inconel 690 to stainless steel of 4:1 is representative of the material surface proportions of a primary circuit, and therefore adequate to simulate the corrosion product output during a Full System decontamination. Oxide thickness on Inconel 600 or Inconel 690 on the samples: between 2 and 3 micrometers; oxide thickness on stainless steel on the samples: between 5 and 8 micrometers.

To ensure comparability, process parameters outside of those compared and explicitly mentioned in the description of the experiment, such as flow, amount of samples and therefore exposed surface and amount of oxide of each material, temperature, etc. are kept constant and identical for all experiments. In addition, the Mn concentrations on the y-xis and the time on the x-axis of Figures 2 to 4 have been normalized relative to each other for better comparability.

Experiment 1

This experiment shows the results obtained from a switch of pH conditions within the oxidation phase without the performance of an intermediate reduction phase, according to the previous state of the art. The evolution of the amount of released corrosion products in solution in relation to the original concentration of oxidant added is presented in **Figure 3**.

Of all three variants, this one has the lowest output of corrosion products in relation to the amount of permanganate injected. The ratio between primary waste and secondary waste is bad, 20%:80%. The time required for application is the lowest of the three experiments.

Experiment 2

This experiment shows the presently applied method for the performance of oxidations under alternating pH conditions. The evolution of the amount of released corrosion products in solution in relation to the original concentration of oxidant added is presented in **Figure 4**. This sequence is significantly more effective and efficient than the sequence according to Experiment 1. The ratio between primary waste and secondary waste is much more advantageous, 50%:50%.

Experiment 3

This experiment shows the application of the method of the present invention. The of the amount of released corrosion products in solution in relation to the original concentration of oxidant added is presented in **Figure 5**. This example according to the invention retains the benefits of Experiment 2 above, with comparable effectiveness and efficiency, while required significantly less time for completion of the application.

CLAIMS

1. A method of decontaminating metal surfaces in a cooling system of a nuclear reactor, wherein the metal surfaces are coated with a solid metal oxide layer including radionuclides, the method comprising at least one treatment cycle, wherein the treatment cycle comprises:
   a) at least two subsequent oxidation steps, wherein one oxidation step comprises:
      a1) contacting the solid metal oxide layer including radionuclides with an aqueous solution comprising a permanganate oxidant,
      a2) contacting unreacted permanganate, if present, and insoluble manganese compounds obtained in step a1) with an aqueous solution of a reducing agent,
      a3) removing solubilized metal oxides and released radionuclides, including solubilized manganese compounds obtained in steps a1) and a2),
   b) a dissolution step, wherein the solid metal oxide layer including radionuclides of step a) is further contacted with an aqueous solution of an organic acid,
   c) a cleaning step, wherein solubilized metal oxides and released radionuclides of step b) are removed.

2. The method of claim 1, wherein for each the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is individually selected from an acidic permanganate oxidant and an alkaline permanganate oxidant.

3. The method of claim 1 or 2, wherein in at least one of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an acidic permanganate oxidant, and in at least one of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an alkaline permanganate oxidant.

4. The method of any of claims 1 to 3, wherein in the first of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an acidic permanganate oxidant.

5. The method of claim 4, wherein in the first two, more preferably the first three, even more preferably the first four, of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an acidic permanganate oxidant.

6. The method of any one of claims 1 to 5, wherein in the last of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an alkaline permanganate oxidant.

7. The method of claim 6, wherein in the last two, more preferably the last three, even more preferably the last four, of the at least two subsequent oxidation steps of a), the permanganate oxidant in step a1) is an alkaline permanganate oxidant.

8. The method of any one of claims 2 to 7, wherein the acidic permanganate oxidant of step a1) is selected from the group consisting of $HMnO_4$, $HMnO_4/HNO_3$, $KMnO_4/HNO_3$, $HMnO_4/H_3PO_4$, $KMnO_4/H_3PO_4$, $KMnO_4$/methane sulfonic acids, $HMnO_4$/methane sulfonic acids, and/or combinations thereof.

9. The method of any one of claims 2 to 8, wherein the alkaline permanganate oxidant of step a1) is selected from $KMnO_4/LiOH$, $KMnO_4/NaOH$, $KMnO_4/KOH$, and/or combinations thereof.

10. The method of any one of claims 2 to 9, wherein the aqueous solution of the acidic permanganate oxidant of step a1) has a pH value of less than 6, preferably less than 4.

11. The method any one of claims 2 to 10, wherein the aqueous solution of the alkaline permanganate oxidant of step a1) has a pH value of at least 8, preferably at least 10.

12. The method any one of claims 1 to 11, wherein the reducing agent of step a2) is selected from the group consisting of oxalic acid, formic acid, glyoxylic acid, citric acid, picolinic acid, ascorbic acid, ethylenediamine-tetraacetic acid, methylsulfonic acid, nitrilotriacetic acid, hydrogen peroxide, hydrazine, hydrogen and/or combinations thereof.

13. The method of any one of claims 1 to 12, wherein step a2) and a3) are performed at least in parts simultaneously, preferably wherein step a2) and a3) are performed entirely simultaneously.

14. The method any one of claims 1 to 13, wherein the organic acid of step b) is selected from the group consisting of oxalic acid, formic acid, glyoxylic acid, citric acid, picolinic

acid, ascorbic acid, ethylenediamine-tetraacetic acid, methylsulfonic acid, nitrilotriacetic acid, and/or combinations thereof.

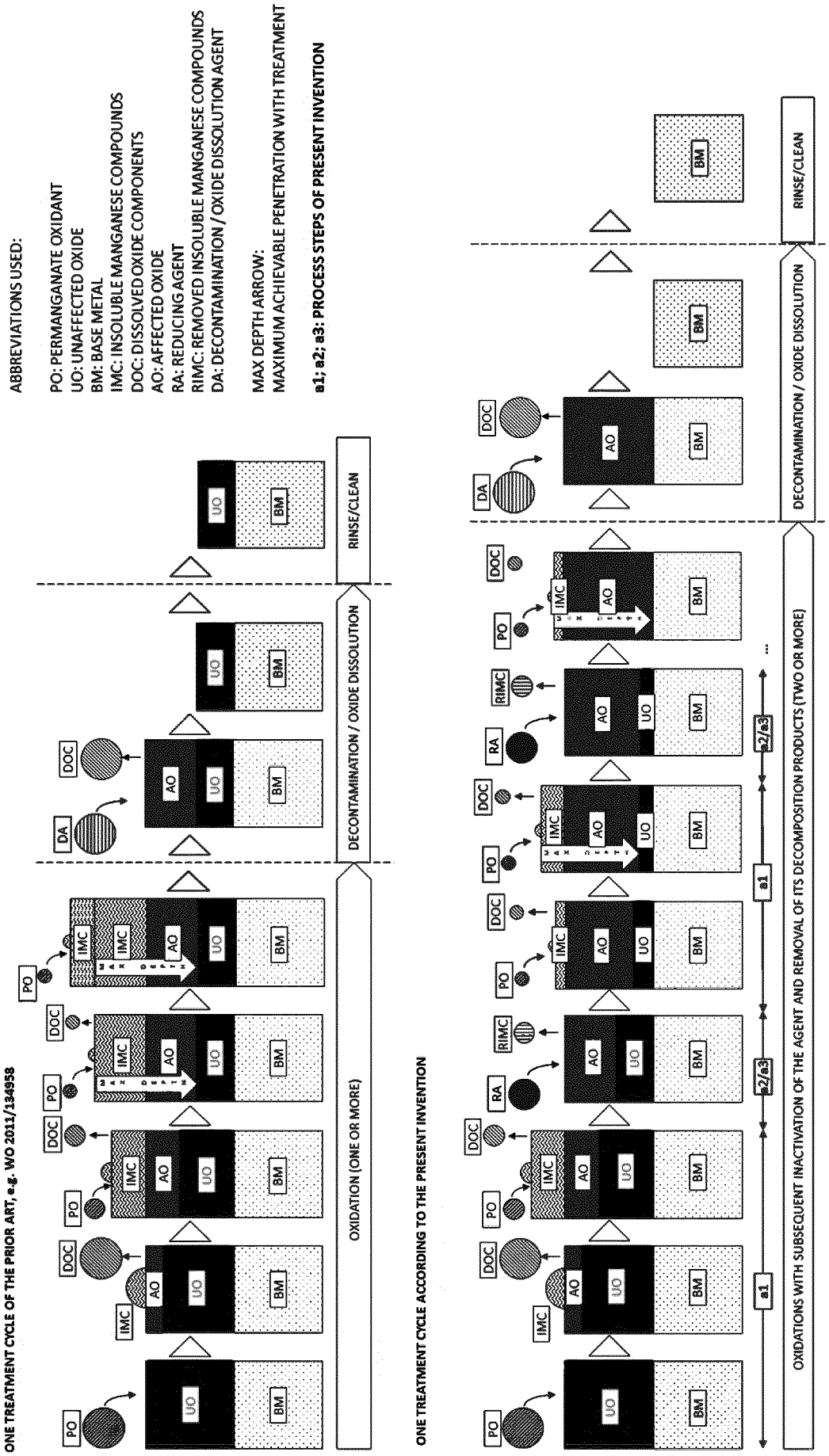

ABBREVIATIONS USED:
PO: PERMANGANATE OXIDANT
UO: UNAFFECTED OXIDE
BM: BASE METAL
IMC: INSOLUBLE MANGANESE COMPOUNDS
DOC: DISSOLVED OXIDE COMPONENTS
AO: AFFECTED OXIDE
RA: REDUCING AGENT
RIMC: REMOVED INSOLUBLE MANGANESE COMPOUNDS
DA: DECONTAMINATION / OXIDE DISSOLUTION AGENT
MAX DEPTH ARROW:
MAXIMUM ACHIEVABLE PENETRATION WITH TREATMENT
a1; a2; a3: PROCESS STEPS OF PRESENT INVENTION
ONE TREATMENT CYCLE OF THE PRIOR ART, e.g. WO 2011/134958
OXIDATION (ONE OR MORE)
DECONTAMINATION / OXIDE DISSOLUTION
RINSE/CLEAN
ONE TREATMENT CYCLE ACCORDING TO THE PRESENT INVENTION
OXIDATIONS WITH SUBSEQUENT INACTIVATION OF THE AGENT AND REMOVAL OF ITS DECOMPOSITION PRODUCTS (TWO OR MORE)
DECONTAMINATION / OXIDE DISSOLUTION
RINSE/CLEAN

FIGURE 1

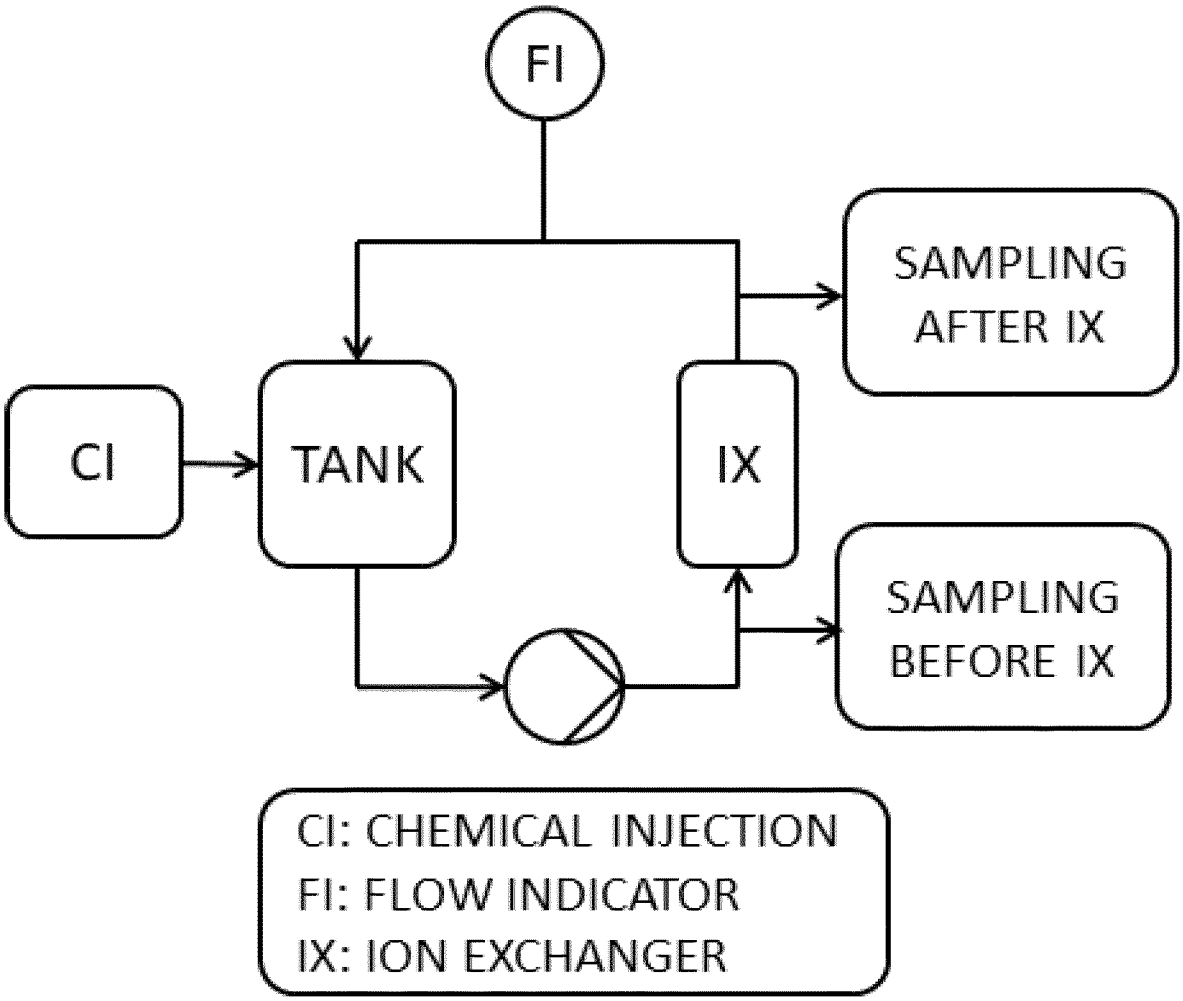

FI
SAMPLING AFTER IX
CI
TANK
IX
SAMPLING BEFORE IX
CI: CHEMICAL INJECTION
FI: FLOW INDICATOR
IX: ION EXCHANGER

FIGURE 2

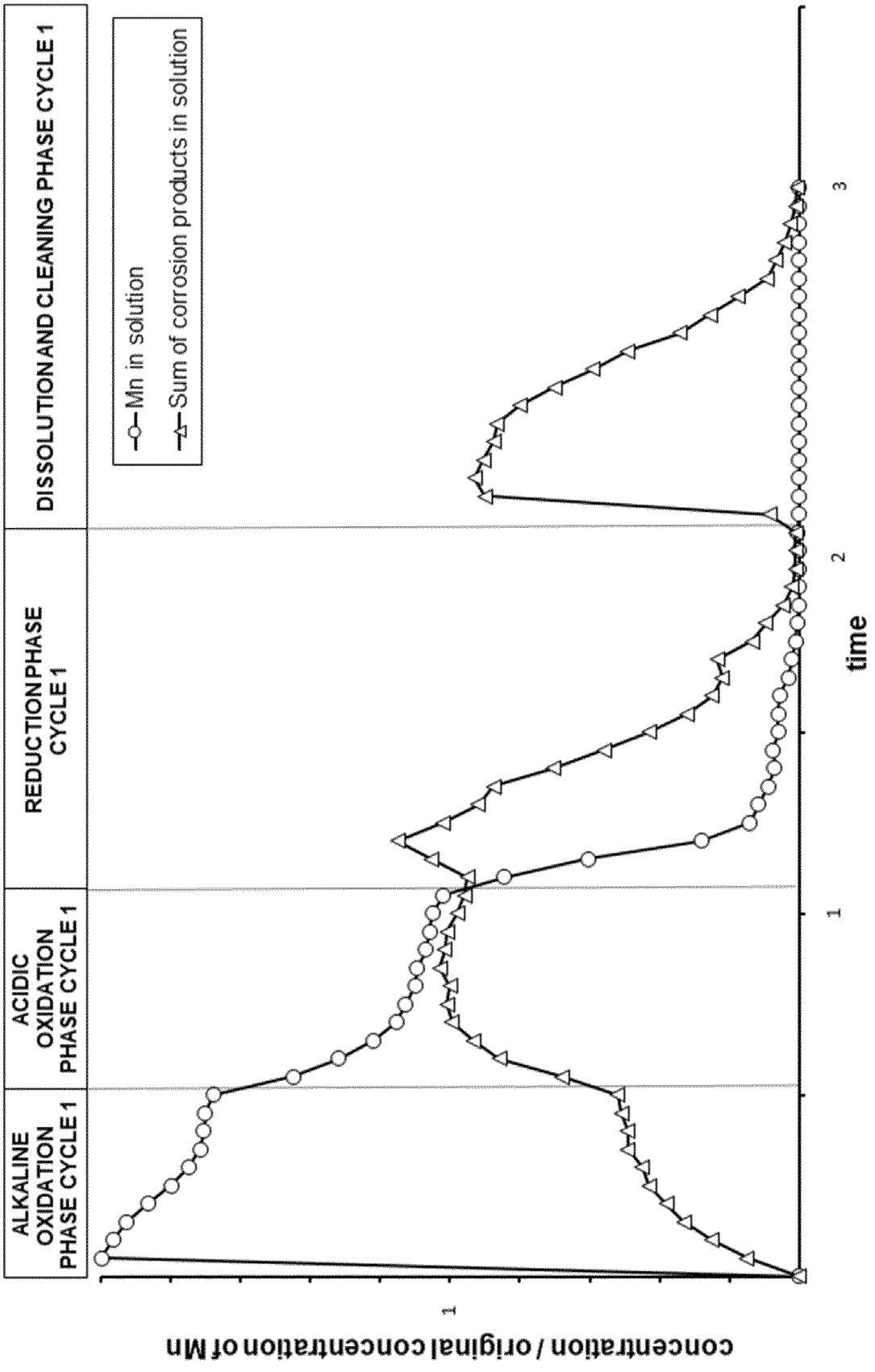

ALKALINE OXIDATION PHASE CYCLE 1
ACIDIC OXIDATION PHASE CYCLE 1
REDUCTION PHASE CYCLE 1
DISSOLUTION AND CLEANING PHASE CYCLE 1
Mn in solution
Sum of corrosion products in solution
concentration / original concentration of Mn
time
1
2
3

FIGURE 3

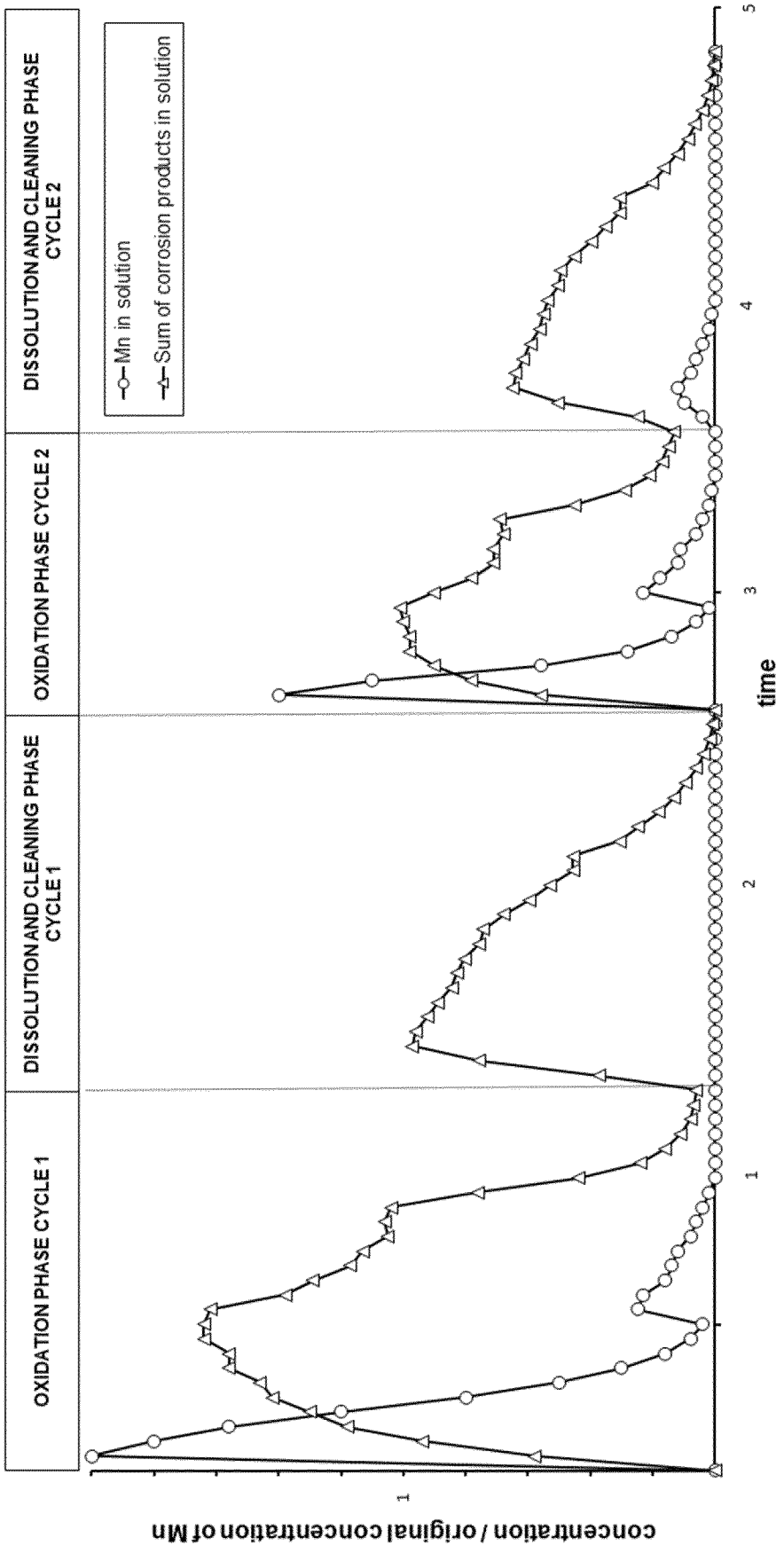

OXIDATION PHASE CYCLE 1
DISSOLUTION AND CLEANING PHASE CYCLE 1
OXIDATION PHASE CYCLE 2
DISSOLUTION AND CLEANING PHASE CYCLE 2
Mn in solution
Sum of corrosion products in solution
concentration / original concentration of Mn
time
1
2
3
4
5

FIGURE 4

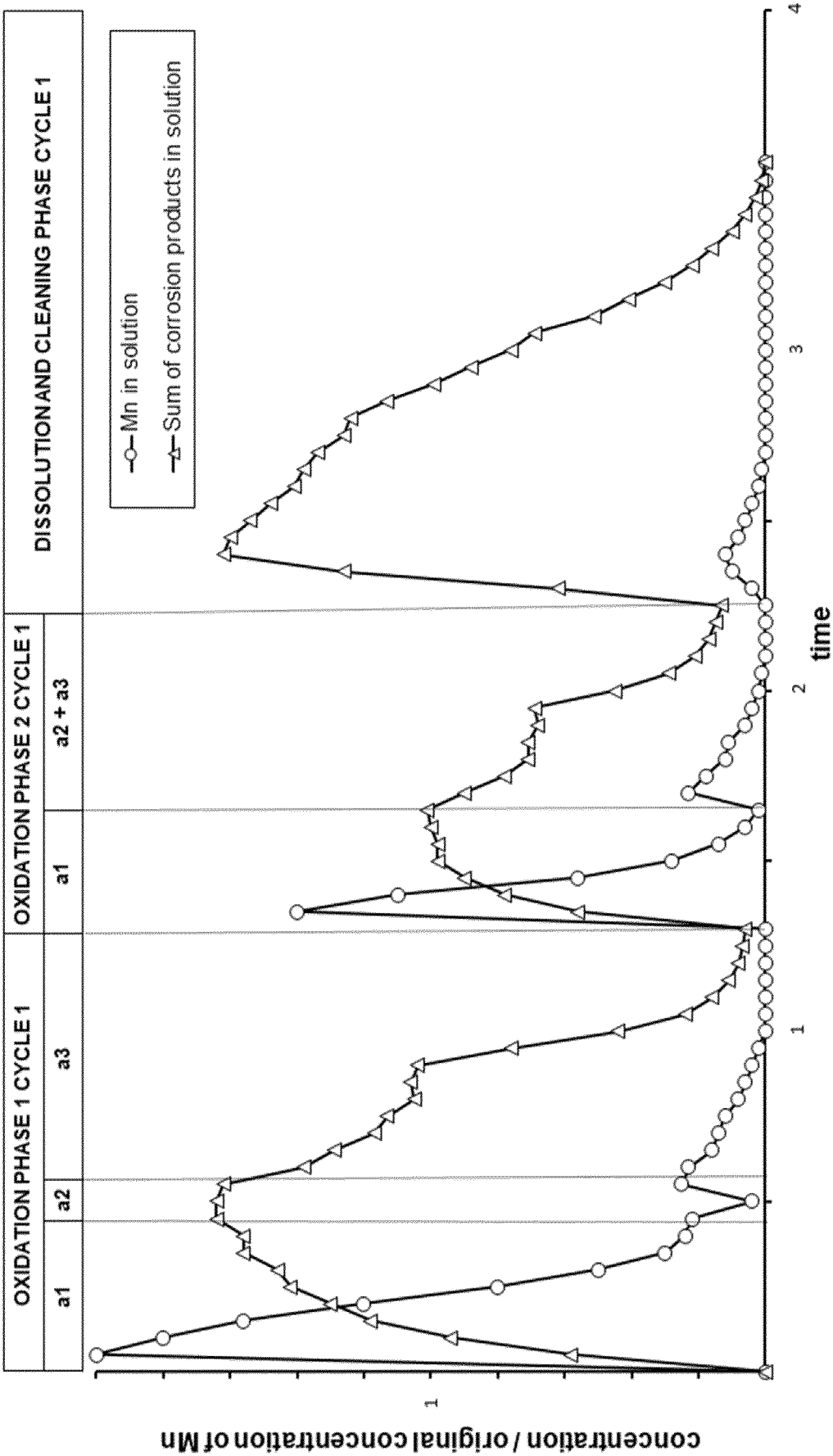

OXIDATION PHASE 1 CYCLE 1
a1
a2
a3
OXIDATION PHASE 2 CYCLE 1
a1
a2 + a3
DISSOLUTION AND CLEANING PHASE CYCLE 1
Mn in solution
Sum of corrosion products in solution
concentration / original concentration of Mn
time
1
2
3
4

FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/076722

A. CLASSIFICATION OF SUBJECT MATTER

INV. G21F9/00 G21F9/30 G21C17/022 C23G1/02 C23G1/14
ADD. G21F9/12

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)

G21F G21C C23G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/220366 A1 (GASSEN RAINER [DE] ET AL) 29 August 2013 (2013-08-29)	1-14
Y	the whole document	13

Y	CA 3 003 488 C (FRAMATOME GMBH [DE]) 14 March 2023 (2023-03-14)	13
A	the whole document	1-12,14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 November 2024	03/12/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Grivas, Symeon

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/076722

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013220366 A1	29-08-2013	CN 102667958 A	12-09-2012
		DE 102010028457 A1	03-11-2011
		EP 2564394 A1	06-03-2013
		ES 2441589 T3	05-02-2014
		JP 2013529299 A	18-07-2013
		KR 20130014494 A	07-02-2013
		TW 201201221 A	01-01-2012
		US 2013220366 A1	29-08-2013
		WO 2011134958 A1	03-11-2011
CA 3003488 C	14-03-2023	AR 106580 A1	31-01-2018
		CA 3003488 A1	11-05-2017
		KR 20180080284 A	11-07-2018
		RO 132891 A2	30-10-2018
		WO 2017076431 A1	11-05-2017