(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 465 308 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
20.11.2024 Bulletin 2024/47

(21) Application number: **23740388.6**

(22) Date of filing: **05.01.2023**

(51) International Patent Classification (IPC):
G21F 9/00 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
G21F 9/00

(86) International application number:
PCT/KR2023/000203

(87) International publication number:
WO 2023/136544 (20.07.2023 Gazette 2023/29)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **14.01.2022 KR 20220006014**

(71) Applicant: **Korea Hydro & Nuclear Power Co., Ltd**
Gyeongju-si, Gyeongsangbuk-do 38120 (KR)

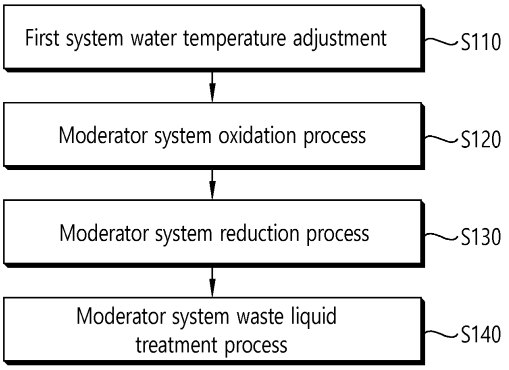
(72) Inventors:
- **KIM, Cho Rong**
  Daejeon 34014 (KR)
- **KIM, Hak Soo**
  Seoul 05310 (KR)
- **KIM, Jeong Ju**
  Gyeryong-si, Chungcheongnam-do 32806 (KR)

(74) Representative: **Habermann, Hruschka & Schnabel**
Patentanwälte
Montgelasstraße 2
81679 München (DE)

(54) SYSTEMIC DECONTAMINATION METHOD OF HEAVY WATER REACTOR

(57) The present invention relates to a systemic decontamination method of a heavy water reactor, the method comprising the steps of: performing decontamination of a moderator system; and performing decontamination of a coolant system after the decontamination of the moderator system, wherein the decontamination of the moderator system is performed by adjusting the temperature of a first system water of the moderator system to a first system water process temperature and sequentially conducting a moderator system oxidation process and a moderator system reduction process.

FIG. 3



Processed by Luminess, 75001 PARIS (FR)

Description

Technical Field

[0001] The present disclosure relates to a systematic decontamination method for a heavy water nuclear reactor.

Background Art

[0002] In a heavy water nuclear reactor, heavy water is used as a moderator for slowing down neutrons and a coolant for absorbing heat energy.

[0003] The development of decommissioning technology and decontamination technology for a heavy water nuclear reactor is required, as in a light water nuclear reactor.

[0004] However, there is no development of technology for systematic decontamination for a heavy water nuclear reactor.

Disclosure

Technical Problem

[0005] Therefore, an object of the present disclosure is to provide a systematic decontamination method for a heavy water nuclear reactor.

Technical Solution

[0006] The object of the present disclosure is achieved by a system decontamination method for a heavy water nuclear reactor, the system decontamination method including: performing decontamination of a moderator system; and performing decontamination of a coolant system after the decontamination of the moderator system, wherein the decontamination of the moderator system is performed by adjusting a temperature of first system water of the moderator system to a first system water process temperature and sequentially performing a moderator system oxidation process and a moderator system reduction process.

[0007] The first system water process temperature may be 65°C to 95°C, and the adjustment of the first system water process temperature may be performed through at least one of a) heating of the first system water using an ultraviolet lamp, and b) use of a heat source of the coolant system.

[0008] The heat source of the coolant system may be provided by using a coolant pump and a heat exchanger of the coolant system.

[0009] In the decontamination of the moderator system, a moderator system waste liquid treatment process may be performed after the moderator system reduction process, and an ultraviolet lamp may be used in the moderator system waste liquid treatment process.

[0010] The decontamination of the coolant system may be performed by adjusting a temperature of second system water of the coolant system to a second system water process temperature and then performing a coolant system reduction process.

[0011] At least one of permanganic acid and potassium permanganate may be used in the moderator system oxidation process, at least one of oxalic acid and citric acid may be used in the moderator system reduction process, a decontamination target in the moderator system oxidation process may include chromium oxide, and a decontamination target in the moderator system reduction process may include at least one of iron oxide and nickel oxide.

[0012] The second system water process temperature may be 90°C to 100°C.

[0013] In the decontamination of the coolant system, a coolant system oxidation process, a coolant system additional reduction process, and a coolant system waste liquid treatment process may be sequentially performed after the coolant system reduction process.

[0014] The system decontamination method may include: measuring a surface dose rate of the coolant system to derive a decontamination factor value, after the coolant system reduction process, and the coolant system oxidation process and the coolant system additional reduction process may be performed when the derived decontamination factor value does not satisfy a target value.

[0015] At least one of citric acid and oxalic acid may be used in the coolant system reduction process, at least one of permanganic acid and potassium permanganate may be used in the coolant system oxidation process, at least one of citric acid and oxalic acid may be used in the coolant system additional reduction process, a decontamination target in the coolant system reduction process may include iron oxide, and a decontamination target in the coolant system oxidation process may include chromium oxide.

Advantageous Effects

[0016] According to the present disclosure, a systematic decontamination method for a heavy water nuclear reactor is provided.

Description of Drawings

[0017]

FIG. 1 is a diagram illustrating a configuration of a moderator decontamination facility that performs a decontamination method of the present disclosure.

FIG. 2 is a diagram illustrating a configuration of a coolant decontamination facility that performs the decontamination method of the present disclosure.

FIG. 3 is a flowchart of a decontamination method for a moderator system according to an embodiment of the present disclosure.

FIG. 4 is a flowchart of a decontamination method for a coolant system according to an embodiment of the present disclosure.

FIG. 5 shows results of an experiment in which an oxide film removal rate of the coolant system depending on a temperature is simulated.

FIG. 6 shows results of an experiment in which an oxide film removal rate of the moderator system depending on a temperature is simulated.

Mode for Disclosure

[0018] In a heavy water nuclear reactor, a moderator system and a coolant system are separated, unlike a light water nuclear reactor.

[0019] The present disclosure provides a decontamination method for each of the moderator system and the coolant system. In particular, the present disclosure proposes a decontamination order and a system-specific decontamination method in which the moderator system is decontaminated first and the coolant system is decontaminated later.

[0020] A decontamination process of the coolant system and the moderator system according to the present disclosure will be described with reference to FIGS. 1 and 2.

[0021] FIG. 1 is a configuration diagram illustrating a configuration of a moderator decontamination facility that performs the decontamination method of the present disclosure, and FIG. 2 is a configuration diagram illustrating a configuration of a coolant decontamination facility that performs the decontamination method of the present disclosure.

[0022] The moderator decontamination facility is connected to the moderator system, and first system water is circulated therein.

[0023] The moderator decontamination facility includes, for example, a filter, a demineralizer, a UV reaction tank, an oxidizing agent manufacturing device, and a chemical injection pump. Although not shown, the moderator decontamination facility may further include a configuration for supplying a reducing agent. Further, in the moderator system, chemicals can be supplied through a calandria.

[0024] For the UV reaction tank, an ultraviolet lamp, particularly, a UVB lamp may be used.

[0025] The coolant decontamination facility is connected to the coolant system, and second system water is circulated therein.

[0026] The coolant decontamination facility includes, for example, a pressure reducing device, a filter, a demineralizer, a UV reaction tank, and an injection pump. Although not shown, the coolant decontamination facility may further include a configuration for supplying a reducing agent and an oxidizing agent.

[0027] For the UV reaction tank, an ultraviolet lamp, particularly, a UVC lamp may be used.

[0028] A decontamination method according to an embodiment of the present disclosure will be described with reference to FIGS. 3 and 4.

[0029] FIG. 3 is a flowchart of a decontamination method for a moderator system according to an embodiment of the present disclosure, and FIG. 4 is a flowchart of a decontamination method for a coolant system according to an embodiment of the present disclosure.

[0030] In the moderator decontamination method, a temperature of the first system water is first adjusted (S110).

[0031] A temperature of the first system water is increased and adjusted to a first system water process temperature. The first system water process temperature may be 65°C to 95°C or 85°C to 95°C.

[0032] The moderator system operates at room temperature at the time of a normal operation. The increase in the temperature of the first system water may be performed using the UV reaction tank or a heat source of the coolant system.

[0033] When the UV reaction tank is used, the ultraviolet lamp may include a UVB lamp.

[0034] When the heat source of the coolant system is used, a temperature of the second system water is increased to 100°C or higher in the coolant system using a coolant pump so that a heat source is generated, and then the generated heat source is transferred to the first system water. Specifically, the heat source of the coolant system is transferred to the inside of the calandria, and the temperature of the moderator system can be increased through the heat transfer.

[0035] Next, a moderator system oxidation process (S120) is performed.

[0036] In the moderator system oxidation process, at least one of permanganic acid, permanganic acid + nitric acid, and potassium permanganate + pH adjuster (the pH adjuster is nitric acid or sodium hydroxide) is used. The moderator system is usually made of stainless steel, and a decontamination target includes chromium oxide or a chromium oxide film.

[0037] Thereafter, a moderator system reduction process (S130) is performed.

[0038] In the moderator system reduction process, organic acid is used, and the organic acid may include at least one of citric acid and oxalic acid. The decontamination target is iron oxide and/or nickel oxide.

[0039] After the decontamination is completed, a moderator system waste liquid treatment process (S140) is performed, and waste liquid treatment may be performed using the UV reaction tank. After the organic acid is removed by using the UV reaction tank, the remaining organic acid may be removed by using an ion exchange resin or an oxidizing agent. For a UV lamp of the UV reaction tank used at this time, a UVC or UVB lamp may be used.

[0040] Thereafter, a surface dose rate of the moderator system is measured for derivation of a decontamination factor (DF), and when the derived DF value does not satisfy a target value, the moderator system oxidation process (S120), the moderator system reduction process (S130), and the moderator system waste liquid treatment process (S140) are repeatedly performed. The decontamination factor is a value derived by using a surface dose rate measurement value of a pipe or the like, and a reference value of the decontamination factor is a specific value in a range of 20 to 40 and may be determined depending on an on-site situation. For the surface dose rate, the surface dose rate of the pipe or the like within the system may be measured using a mobile or fixed radiation meter.

[0041] After the decontamination of the moderator system is completed, the decontamination of the coolant system is performed.

[0042] In the coolant system decontamination, the temperature of the second system water is first adjusted (S210).

[0043] The temperature of the second system water is adjusted to a second system water process temperature. The temperature adjustment is performed using a coolant pump and a shutdown cooling heat exchanger, and the second system water process temperature may be 90°C to 100°C.

[0044] When the temperature of the first system water is adjusted by the heat source of the coolant system, the temperature of the second system water only needs to be slightly decreased after the use as the heat source, making the process simpler and efficient treatment possible. For example, when the temperature of the second system water is increased to 100°C for generation of a heat source for the adjustment of the temperature of the first system water, the decontamination of the coolant system can be performed immediately by slightly reducing the temperature of the second system water to 95°C.

[0045] Thereafter, a coolant system reduction process (S220) is performed. In the coolant system reduction process, organic acid is supplied, and the organic acid includes at least one of citric acid and oxalic acid. The coolant system is mainly made of carbon steel, and the decontamination target includes iron oxide or an iron oxide film. A concentration of the organic acid may be 500 to 1,000 ppm or 500 to 2,000 ppm.

[0046] Thereafter, a surface dose rate of the coolant system is measured for derivation of a decontamination factor (DF), and when the derived DF value does not satisfy a target value, a coolant system oxidation process (S230) and a coolant system additional reduction process (S240) are performed. The decontamination factor is a value derived by using a surface dose rate measurement value of a pipe or the like, and a target reference value of the decontamination factor may be determined as a specific value in a range of 20 to 40. For the surface dose rate, the surface dose rate of the pipe or the like within the system may be measured using a mobile or fixed radiation meter.

[0047] The surface dose rate of the coolant system is measured, and when the decontamination factor satisfies the target reference value, the coolant system oxidation process (S230) and the coolant system additional reduction process (S240) are omitted, and a coolant system waste liquid treatment process (S250) is performed.

[0048] The coolant system oxidation process (S230) and the coolant system additional reduction process (S240) that are selectively performed may be performed when chromium oxide is generated due to a steam generator pipe made of Alloy 800 and it is difficult to remove all of the oxide film through the reduction process.

[0049] In the coolant system oxidation process (S230), at least one of permanganic acid, permanganic acid + nitric acid, and potassium permanganate + pH adjuster (the pH adjuster is nitric acid or sodium hydroxide) is used. A target of the decontamination is the chromium oxide (chromium oxide film). A large amount of oxidizing agent may be used so that the decomposition of the organic acid remaining in the reduction process, and the oxidation process are simultaneously performed. This oxidation process is performed after the reduction process in consideration of a problem that the permanganic acid is self-decomposed by carbon steel and deposits are formed.

[0050] In the coolant system additional reduction process (S240), the permanganic acid remaining after the oxidation process is decomposed into organic acid. Further, in the present process, the iron oxide (iron oxide film) and/or nickel oxide (nickel oxide film) present under the chromium oxide film can be removed. A large amount of oxidizing agent may be used so that the decomposition of the remaining permanganic acid and the reduction process can be simultaneously performed. For the organic acid, oxalic acid or citric acid may be used.

[0051] Thereafter, the coolant system waste liquid treatment process (S250) is performed. The coolant system waste liquid treatment process may be performed using the UV reaction tank. After the organic acid is removed by using the UV reaction tank, the remaining organic acid may be removed by using an ion exchange resin or an oxidizing agent. For the ultraviolet lamp of the UV reaction tank used at this time, a UVB lamp or a UVC lamp may be used.

[0052] FIG. 5 shows results of an experiment in which an oxide film removal rate of a coolant system depending on a temperature is simulated, and FIG. 6 shows results of an experiment in which an oxide film removal rate of a moderator system depending on a temperature is simulated.

[0053] Experimental conditions and experiment method of the coolant system are as follows.

[0054] Using carbon steel, a simulated specimen was immersed in citric acid (1L) of 0.1% for 8 hours and then the experiment was performed at a temperature of 60 to 95°C. After the experiment was performed, weights of the simulated specimen before and after the decontamination were measured for derivation of the oxide film removal rate.

[0055] Experimental conditions and experiment method of the moderator system are as follows.

[0056] Using stainless steel, the oxidation process and the reduction process were performed for a total of eight hours, each four hours. In this case, in the oxidation process, permanganic acid + nitric acid was used for the experiment, and in the reduction process, oxalic acid was used. After the experiment was performed, weights of the simulated specimen before and after the decontamination were measured for derivation of the oxide film removal rate.

[0057] Experimental results showed that the oxide film removal rate of 100% or more was shown at 70°C or more in the case of the carbon steel as shown in FIG. 5, and the oxide film removal rate of 70% or more was shown at 80°C or more in one cycle, but the highest removal rate was shown at 95°C after two cycles in the case of stainless steel, as shown in FIG. 6. Therefore, it is necessary to perform systematic decontamination between 70°C and 95°C in the coolant system, and it is necessary to perform systematic decontamination at 80°C or more in the moderator system.

[0058] The above-described embodiments are examples for describing the present disclosure, and the present disclosure is not limited thereto. Since those skilled in the art to which the present disclosure pertains will be able to implement the present disclosure through various modifications of the embodiments, the technical protection scope of the present disclosure should be determined by the appended claims.

Claims

1. A system decontamination method for a heavy water nuclear reactor, the system decontamination method comprising:

    performing decontamination of a moderator system; and
    performing decontamination of a coolant system after the decontamination of the moderator system, wherein
    the decontamination of the moderator system is performed by adjusting a temperature of first system water of the moderator system to a first system water process temperature and sequentially performing a moderator system oxidation process and a moderator system reduction process.

2. The system decontamination method of claim 1, wherein

    the first system water process temperature is 65°C to 95°C, and
    the adjustment of the first system water process temperature is performed through at least one of

    a) heating of the first system water using an ultraviolet lamp, and
    b) use of a heat source of the coolant system.

3. The system decontamination method of claim 2, wherein the heat source of the coolant system is provided by using a coolant pump and a heat exchanger of the coolant system.

4. The system decontamination method of claim 1, wherein

    in the decontamination of the moderator system, a moderator system waste liquid treatment process is performed after the moderator system reduction process, and
    an ultraviolet lamp is used in the moderator system waste liquid treatment process.

5. The system decontamination method of claim 1, wherein the decontamination of the coolant system is performed by adjusting a temperature of second system water of the coolant system to a second system water process temperature and then performing a coolant system reduction process.

6. The system decontamination method of claim 1, wherein

    at least one of permanganic acid and potassium permanganate is used in the moderator system oxidation process,
    at least one of oxalic acid and citric acid is used in the moderator system reduction process,
    a decontamination target in the moderator system oxidation process includes chromium oxide, and
    a decontamination target in the moderator system reduction process includes at least one of iron oxide and nickel oxide.

7. The system decontamination method of claim 6, wherein the second system water process temperature is 90°C to 100°C.

8. The system decontamination method of claim 1, wherein
in decontamination of the coolant system, a coolant system oxidation process, a coolant system additional reduction process, and a coolant system waste liquid treatment process are sequentially performed after the coolant system reduction process.

9. The system decontamination method of claim 8, comprising:

    measuring a surface dose rate of the coolant system to derive a decontamination factor value, after the coolant system reduction process, and the coolant system oxidation process and the coolant system additional reduction process are performed when the derived decontamination factor value does not satisfy a target value.

10. The system decontamination method of claim 8, wherein

at least one of citric acid and oxalic acid is used in the coolant system reduction process, at least one of permanganic acid and potassium permanganate is used in the coolant system oxidation process,
at least one of citric acid and oxalic acid is used in the coolant system additional reduction process,
a decontamination target in the coolant system reduction process includes iron oxide, and
a decontamination target in the coolant system oxidation process includes chromium oxide.

FIG. 1

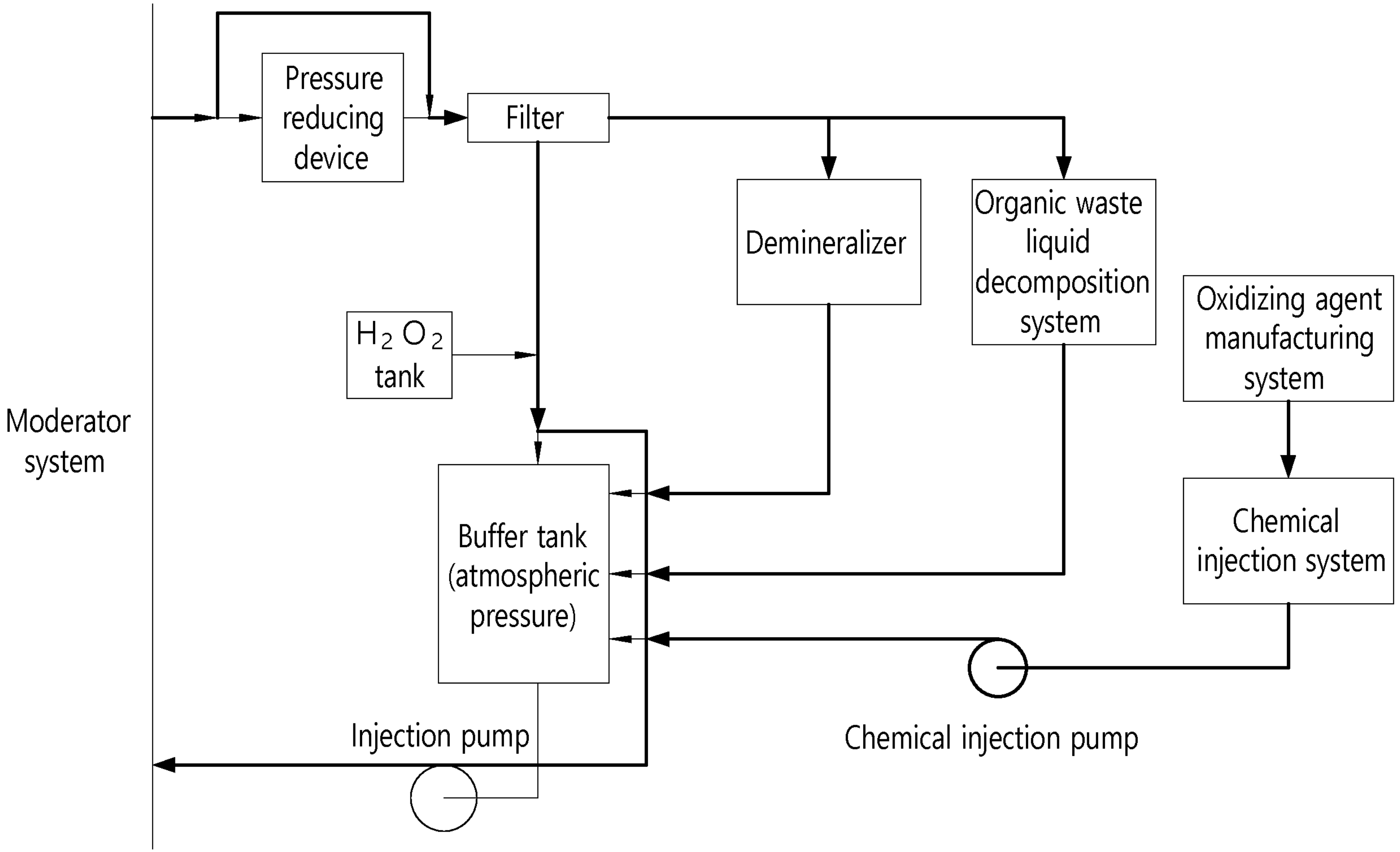

Moderator system
Pressure reducing device
Filter
H_2O_2 tank
Demineralizer
Organic waste liquid decomposition system
Oxidizing agent manufacturing system
Chemical injection system
Buffer tank (atmospheric pressure)
Injection pump
Chemical injection pump

FIG. 2

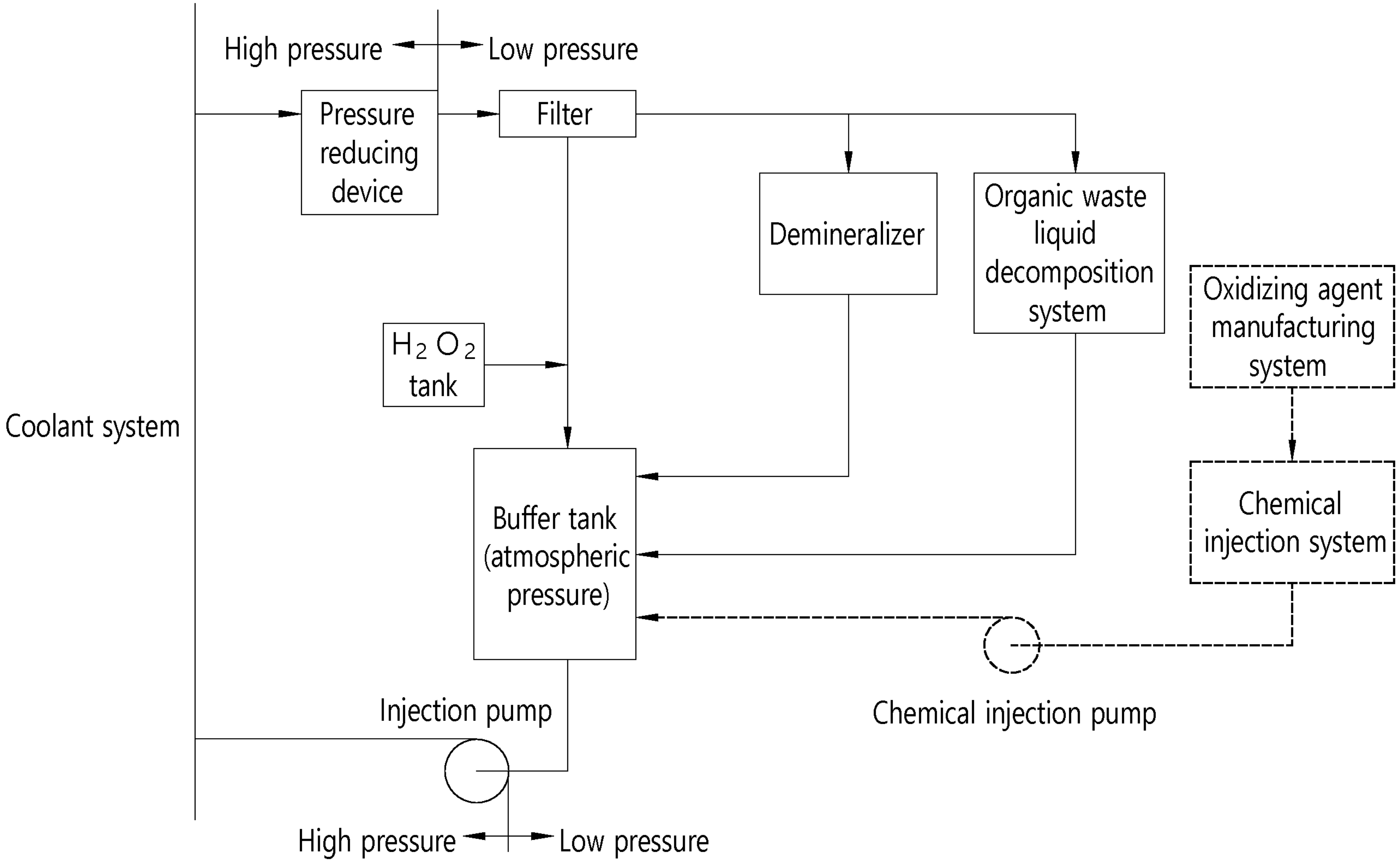

High pressure
Low pressure
Pressure reducing device
Filter
Demineralizer
Organic waste liquid decomposition system
Oxidizing agent manufacturing system
H_2O_2 tank
Coolant system
Buffer tank (atmospheric pressure)
Chemical injection system
Injection pump
Chemical injection pump
High pressure
Low pressure

FIG. 3

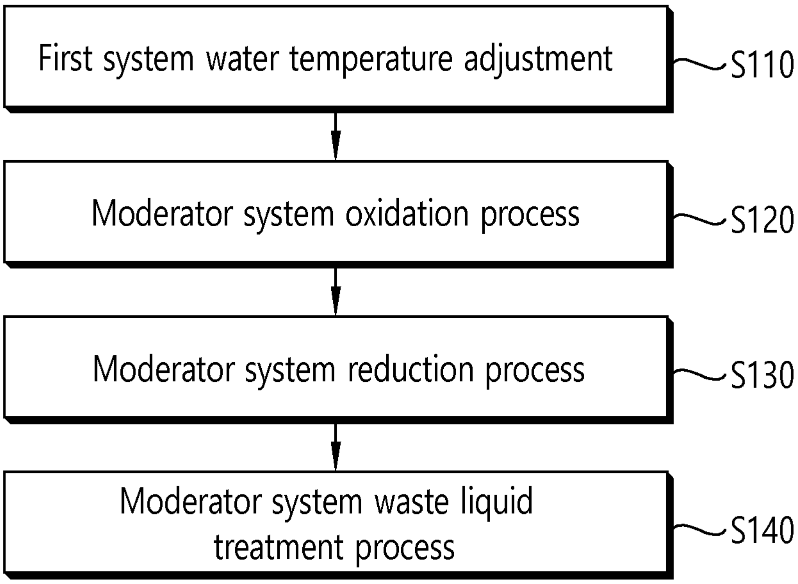

First system water temperature adjustment
S110
Moderator system oxidation process
S120
Moderator system reduction process
S130
Moderator system waste liquid treatment process
S140

FIG. 4

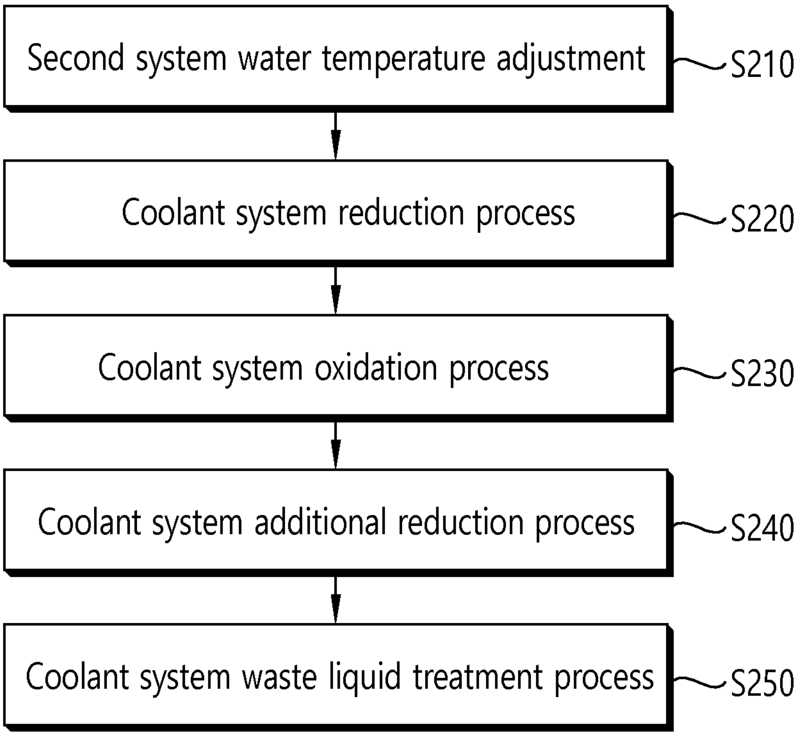

Second system water temperature adjustment
S210
Coolant system reduction process
S220
Coolant system oxidation process
S230
Coolant system additional reduction process
S240
Coolant system waste liquid treatment process
S250

FIG. 5

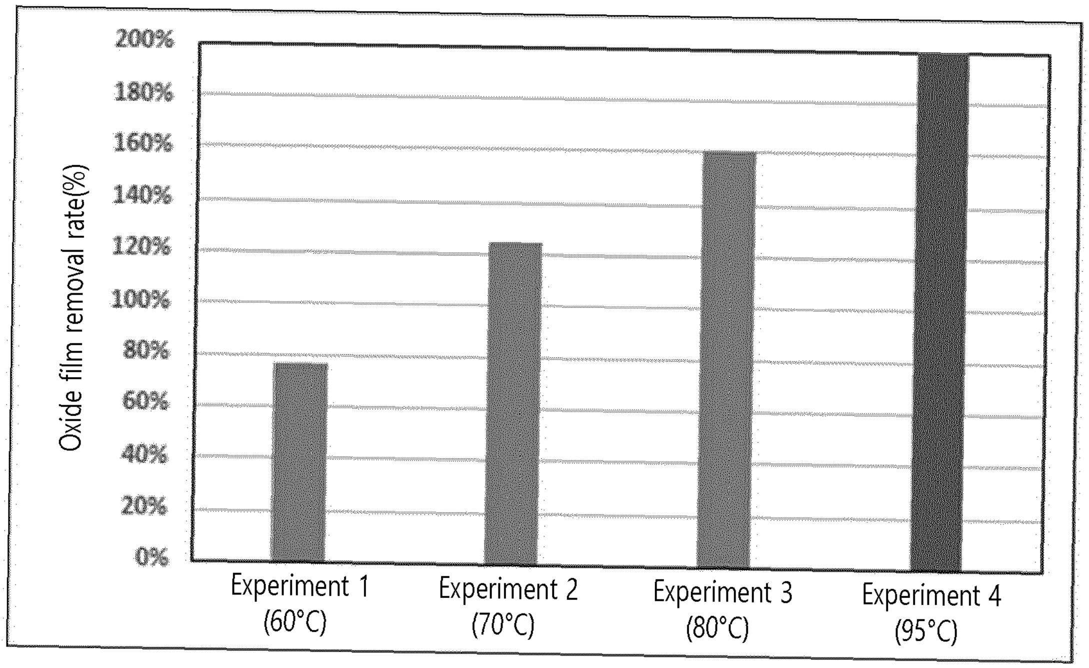
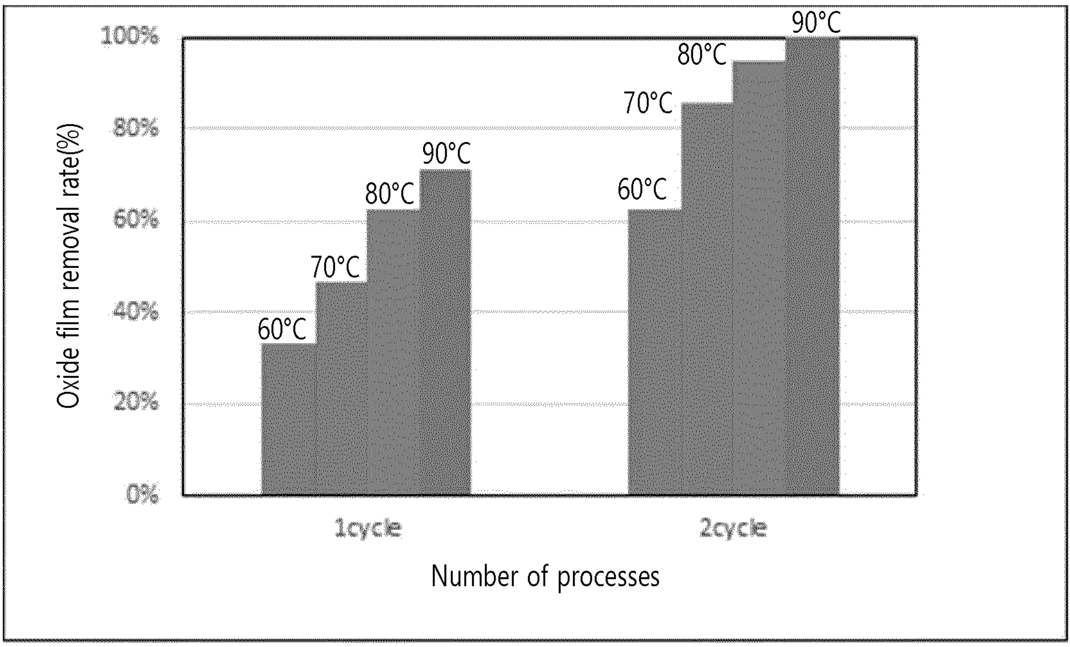

200%
180%
160%
140%
120%
100%
80%
60%
40%
20%
0%
Oxide film removal rate(%)
Experiment 1 (60°C)
Experiment 2 (70°C)
Experiment 3 (80°C)
Experiment 4 (95°C)

FIG. 6


100%
80%
60%
40%
20%
0%
Oxide film removal rate(%)
60°C
70°C
80°C
90°C
60°C
70°C
80°C
90°C
1cycle
2cycle
Number of processes

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2023/000203

A. CLASSIFICATION OF SUBJECT MATTER

G21F 9/00(2006.01)i

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 9/00(2006.01); B01D 15/36(2006.01); G21F 9/06(2006.01); G21F 9/12(2006.01); G21F 9/28(2006.01)

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

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 제염(decontamination), 감속재(moderator), 온도(temperature), 환원(reduction)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	KR 10-2018-0080284 A (FRAMATOME GMBH) 11 July 2018 (2018-07-11) See paragraphs [0007], [0047] and [0109]-[0161]; and figures 1-2.	1-2,4,8-9 5-7,10 3
Y	JP 2009-216577 A (HITACHI-GE NUCLEAR ENERGY LTD.) 24 September 2009 (2009-09-24) See paragraph [0049]; and claim 1.	5,7
Y	KR 10-2019-0015525 A (FRAMATOME GMBH) 13 February 2019 (2019-02-13) See paragraphs [0064] and [0100]; and claim 1.	6-7,10
A	JP 2019-002825 A (HITACHI-GE NUCLEAR ENERGY LTD.) 10 January 2019 (2019-01-10) See entire document.	1-10

☑ 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
"D" document cited by the applicant in the international application
"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 **17 April 2023**	Date of mailing of the international search report **17 April 2023**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208** Facsimile No. **+82-42-481-8578**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2023/000203

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-2006015 B1 (KOREA HYDRO & NUCLEAR POWER CO., LTD.) 31 July 2019 (2019-07-31) See entire document.	1-10

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2023/000203

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
KR 10-2018-0080284 A	11 July 2018	AR 106580 A1	31 January 2018
		CA 3003488 A1	11 May 2017
		RO 132891 A2	30 October 2018
		RO 132891 B1	26 February 2021
		WO 2017-076431 A1	11 May 2017
JP 2009-216577 A	24 September 2009	JP 5091727 B2	05 December 2012
KR 10-2019-0015525 A	13 February 2019	AR 110903 A1	15 May 2019
		CN 109416950 A	01 March 2019
		EP 3446316 A1	27 February 2019
		EP 3446316 B1	15 April 2020
		ES 2795002 T3	20 November 2020
		JP 2019-529877 A	17 October 2019
		JP 6752358 B2	09 September 2020
		KR 10-2122163 B1	12 June 2020
		MX 2018015169 A	10 June 2019
		MX 370759 B	13 December 2019
		US 11443863 B2	13 September 2022
		US 2021-0225543 A1	22 July 2021
		WO 2018-134067 A1	26 July 2018
JP 2019-002825 A	10 January 2019	None	
KR 10-2006015 B1	31 July 2019	KR 10-2035853 B1	23 October 2019