



- (51) **International Patent Classification:**  
C02F 1/66 (2006.01) C02F 103/02 (2006.01)
- (21) **International Application Number:**  
PCT/NL2014/050341
- (22) **International Filing Date:**  
28 May 2014 (28.05.2014)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**  
2010885 29 May 2013 (29.05.2013) NL
- (71) **Applicant:** STICHTING DIENST LANDBOUWKUN-  
DIG ONDERZOEK [NL/NL]; Droevendaalsesteeg 4, NL-  
6708 PB Wageningen (NL).
- (72) **Inventor:** FOEKEMA, Edwin Matheus; Plevierstraat 68,  
NL-1742 AP Schagen (NL).
- (74) **Agents:** JANSEN, C.M. et al.; V.O., Johan de Wittlaan 7,  
NL-2517 JR Den Haag (NL).
- (81) **Designated States** (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,  
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,  
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,  
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,  
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,  
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,  
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,  
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,  
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,  
ZW.

- (84) **Designated States** (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,  
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,  
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,  
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,  
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
KM, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report (Art. 21(3))



WO 2014/193230 A1

(54) **Title:** COOLING WATER

(57) **Abstract:** The invention relates to environmentally friendly methods of reducing and/or preventing fouling on a surface of a component that is in contact with water. The invention further relates to a cooling system that is suited for employing the methods of the invention, and to a power plant, comprising such cooling system.

Title: COOLing water

Field: The invention relates to methods and means of reducing and/or preventing fouling on a surface of a component that is in contact with water.

5

### Introduction

Thermoelectric power plants boil water to create steam, which then spins turbines to generate electricity. The heat used to produce steam can come from burning of a fuel, from nuclear reactions, or directly from the sun or geothermal heat sources underground. Once steam has passed through a turbine, it must be cooled before it can be reused to produce more electricity. This cooling of the primary water circuit is generally achieved by a separate cooling water system that consists of a condenser, a cooling tower, and a cooling water pump. The cooling water is either extracted from a nearby water source and discharged back into this source, or cooled down and recirculated for reuse as cooling water after cooling of the primary water circuit.

A first cooling system is also termed a once-through system. Such system takes water from a nearby source (e.g., river, lake, or ocean), circulates it through pipes to absorb heat from the steam in systems called condensers, and discharges the now warmer water to the local source. Once-through systems were initially the most popular because of their simplicity, low cost, and the possibility of situating power plants in places with abundant supplies of cooling water.

25 A second cooling system is a closed-loop system, also termed a wet-recirculating system. Such system reuses cooling water in a second cycle rather than immediately discharging it back to the original water source. Most commonly, wet-recirculating systems use cooling towers to expose water to ambient air. Some of the water evaporates; the rest is then returned to the condenser in the power plant. Because wet-recirculating systems only withdraw water to replace any water that is lost through evaporation in the cooling tower, these systems have much lower water withdrawals than once-through systems.

30

Fouling of a water system, for example a cooling water system, is a major problem for the industry, for example for power plants. Methods for reducing fouling include the addition of a biocide such as, for example, chlorine to the water. However, chlorination is associated with high costs and environmental concerns due to the generation of chloromethanes and other organochlorines as by-products. Most countries, including European countries, have introduced measures to reduce the discharge of organochlorines into the aquatic environment. Because of these measures, alternative chemical products, such as peracetic acid, are replacing chlorine. However, there is still a need for a more environmentally-friendly and cheap agent that prevents fouling on the surface of a water system.

Therefore, the invention provides a method of reducing and/or preventing fouling on a surface of a component that is in contact with water, the method comprising: transferring carbon dioxide to the water to bring the water at a pH of at most 7.5, whereby the water is not pressurized. Said water preferably is fresh water, for example fresh cooling water that is used in a power plant.

The term “fresh water” includes surface water such as sea water, brackish water, river water, lake water, and ground water. Said water preferably is salt water, preferably seawater.

Fouling is the accumulation of unwanted material on solid surfaces to the detriment of function. Fouling is distinguished from other surface-growth phenomena in that it occurs on a surface of a component, system or plant performing a defined and useful function, and that the fouling process impedes or interferes with this function. The fouling material can consist of either living organisms (biofouling) or non-living substances including, for example, scaling.

Biofouling is the accumulation of micro-organisms (e.g. algae and diatoms), plants, and animals on surfaces. Bacteria can form biofilms or slime layers. The organisms aggregate on surfaces using colloidal hydrogels of water and

extracellular polymeric substances such as polysaccharides, lipids, and nucleic acids. Amongst the larger animals that cause widespread fouling are zebra mussel in freshwater, and blue mussel and oyster in seawater.

- 5 Scaling, or precipitation fouling, is the undesirable accumulation of solid salts, oxides and hydroxides from water. These include, for example, calcium carbonate and calcium sulfate. Scale deposits are formed by precipitation and crystal growth at a surface in contact with water. The most common scale-forming salts that deposit on heat transfer surfaces are those that exhibit retrograde solubility  
10 with temperature. Although they may be completely soluble in the lower-temperature bulk water, these compounds (e.g., calcium carbonate, calcium phosphate, and magnesium silicate) supersaturate in the higher-temperature water adjacent to the heat transfer surface and precipitate on the surface. Metallic surfaces are ideal sites for crystal nucleation because of their rough  
15 surfaces and the low velocities adjacent to the surface. Corrosion cells on the metal surface produce areas of high pH, which promote the precipitation of many cooling water salts. Once formed, scale deposits initiate additional nucleation, and crystal growth proceeds at an accelerated rate.
- 20 The addition of carbon dioxide to water to prevent biofouling is known from United States Patent 6,821,442. As described herein, carbon dioxide is transferred to water to supersaturate the water with dissolved carbon dioxide such that aquatic species are killed. For this supersaturation, the water is contained within a closed system and pressurized such that delta P is greater  
25 than 0.0 mm Hg. Delta P is calculated as:

$$\text{Delta P} = pN_2 + pO_2 + pH_2O + pCO_2 - p\text{Atm},$$

whereby  $pN_2$  includes argon and other trace atmospheric gasses.

- 30 It is noted in US6,821,442 that supersaturation of water with carbon dioxide would induce gas bubble trauma (GBT), which may result in the killing of aquatic species.

The present inventor now established that the transfer of carbon dioxide to water at a level such that delta P is below atmospheric pressure prevents growth of young shellfish, prevents scaling and results in distraction of fish. Surprisingly, the inventor established that transfer of carbon dioxide to a level such that the pH of the water is at most 7.5, is sufficient for prevention, or at least for reduction, of fouling on a surface of a component that is in contact with said water. The transfer of carbon dioxide to water at a level such that the pH of the water is at most 7.5, provides an environmentally-friendly and cheap agent to prevent fouling on the surface of a cooling water system. Carbon dioxide is a natural gas essential for life. Within the limits that are sufficient to reduce fouling, the elevated concentrations of carbon dioxide and consequently reduced pH levels will not result in acute killing of aquatic species, but will rather reduce propagation and reproduction.

Said carbon dioxide is preferably transferred at an intake point of the water. Said water preferably is fresh water, including surface water such as sea water, river water and lake water, and ground water. Said fresh water preferably is salt water, preferably seawater.

The pH of the water is preferably reduced to a pH of between 6.0 and 7.5, such as to a pH of 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 6.95, 7.0, 7.1, 7.2, 7.3 7.4 or 7.5. The pH is preferably not below 6, more preferably not below 6.5 in order not to cause damage to the water system such as corrosion of metal components. The pH of the water is therefore preferably between 6.5 and 7.5, such as 6.5, 6.6, 6.7, 6.8, 6.9, 6.95, 7.0, 7.1, 7.2, 7.3 7.4 or 7.5.

Sea water has, on average, a pH of about 8.5. To reduce the pH of sea water to a level of about 7.5, about 10 mg of CO<sub>2</sub> is required per liter of water. To reduce the pH of sea water to a level of about 6.0, about 150 mg of CO<sub>2</sub> is required per liter of water. Hence, the amount of CO<sub>2</sub> that is required per liter of water to adjust the pH of the water to a value of between 6.0 and 7.5 is between

10 and 150 mg. This amount of CO<sub>2</sub> can be transferred to water using methods and means that are known in the art.

A pH of at most 7.5 will increase carbonate solubility and in this way effectively prevent shell fish such as cockles, mussels, and oysters, and other mollusc larvae from forming the shells necessary to settle and survive in the water system. In addition, the increased carbonate solubility of the water results in decreased scaling, while the increased carbon dioxide concentration results in deterrence of fish.

10

To reduce the pH of the cooling water of a plant that consumes about 213.120 m<sup>3</sup>/hr of cooling water to a pH of about 7 requires the addition of about 2771 kg/hr of CO<sub>2</sub>. To reduce the pH of the cooling water of a plant that consumes about 213.120 m<sup>3</sup>/hr of cooling water to a pH of about 6 requires the addition of about 29411 kg/hr of CO<sub>2</sub>. An example of such plant is the Amer power plant in Geertruidenberg, the Netherlands, which has a capacity of about 1245 megawatts. It is further preferred that the carbon dioxide that is transferred to the water to bring the water at a pH of at most 7.5, is produced by the industrial plant that is cooled with the water. An average power plant, for example a NUON multifuel power plant in the Netherlands, produces about 571429 kg of CO<sub>2</sub> per hour. The amount of CO<sub>2</sub> that is transferred to the water to adjust the pH to a level between 6 and 7.5, more preferred to a level between 6.5 and 7.5, is between about 5% and 10% of the total CO<sub>2</sub> emission of the plant.

20

25

The carbon dioxide is optionally treated, for example filtered, prior to transferring the carbon dioxide to the water to reduce or eliminate toxic substances. The carbon dioxide that is included in the exhaust gas from a plant, for example a power plant, may contain toxic substances such as fine particulate matter and metals, for example lead and arsenic. Methods, for example filtration technologies, that are used to remove these toxic substances are known in the art and include scrubbers, such as wet and dry scrubbers.

30

The invention further provides a cooling system comprising means for transferring carbon dioxide to the cooling water to bring the cooling water at a pH of at most 7.5, wherein the cooling water is not pressurized. Said cooling system is preferably for cooling of an industrial plant, for example a power plant, or other industrial plant such as, for example, a chemical plant including a petroleum refinery and a blast furnace.

Said means for transferring carbon dioxide to the water, preferably cooling water, include means for transferring exhaust gas from a plant, preferably filtered exhaust gas, through the water, for example by an exhaust gas discharging chamber for discharging gas in the form of gas bubbles into said water. Said exhaust gas discharging chamber preferably comprises a porous membrane whereby gas absorption rate is enhanced by a bubble dispersion mechanism.

The cooling water may be recycled through a recirculating system or used in a single pass once-through cooling system. In one embodiment, a preferred cooling system according to the invention is a once-through cooling system. The main advantages of a once-through system is that it is a simple type of system and very flexible.

In another embodiment, a preferred cooling system according to the invention is a recirculating system. Recirculating systems may be open if they rely upon cooling towers or cooling ponds to remove heat. If heat removal is accomplished with negligible evaporative loss of cooling water, the recirculating system may be closed. A preferred cooling system, for example for an energy plant is an open recirculating cooling system. Open recirculating cooling systems save a tremendous amount of fresh water compared to the alternative method, once-through cooling. The quantity of water discharged to waste is greatly reduced in the open recirculating method, and chemical treatment is more economical.

However, cooling by evaporation increases the dissolved solids concentration in the water, raising corrosion and deposition tendencies. In addition, the relatively higher temperatures significantly increase corrosion potential and increase the

tendency for biological growth. The transfer of carbon dioxide to the cooling water of an open recirculating cooling system to bring the water at a pH of at most 7.5, preferably at a pH of between 6.5 and 7.5, whereby the water is not pressurized, provides a very economical method of reducing or preventing both scaling and  
5 biological growth.

In a preferred cooling system according to the invention, the cooling water is cooled prior to discharging the cooling water back into its source, or prior to its reuse as cooling water. Cooling of the used cooling water is accomplished, for  
10 example by a cooling tower. A cooling tower is designed to provide intimate air/water contact. Heat rejection is primarily by evaporation of part of the cooling water. Some sensible heat loss (direct cooling of the water by the air) also occurs, but it is only a minor portion of the total heat rejection. Said cooling tower preferably is a natural or mechanical draft tower and the direction of airflow,  
15 relative to the water flow is either counterflow or crossflow. A cooling tower may further aid in reducing the amount of carbon dioxide in the cooling water, prior to discharging the cooling water, for example back into its source.

The invention further provides an industrial plant, for instance a power plant,  
20 and/or a chemical plant including a petroleum refinery and a blast furnace, comprising a cooling system according to the invention. Said plant comprises means for transferring carbon dioxide to the cooling water to bring the cooling water at a pH of at most 7.5, preferably at a pH between 6.5 and 7.5, wherein the cooling water is not pressurized.



## Figure legends

### Figure 1

pH in the water columns of the experimental ecosystems. CO<sub>2</sub> was applied from  
5 day 0 onwards.

Figure 2: Number of juvenile bivalves (*Cerastoderma edule*) in sediment samples  
at the end of the study 69 days after the start of the CO<sub>2</sub> application.

10 Figure 3: Biomass (measured as chlorophyll-a fluorescence, by means of a Biotek  
microtiter plate reader with Gen5 software) of algae settled on substrates at the  
end of the study 69 days after the start of the CO<sub>2</sub> application. Series A and B  
depict substrates at two different positions in the experimental ecosystem.

## Examples

### Example 1

Experiments were performed wherein experimental marine ecosystems were exposed to a series of elevated CO<sub>2</sub>-concentrations. The experiments were conducted in outdoor tanks with a total volume of about 5 m<sup>3</sup> containing natural seawater and sediment inhabited by a community of planktonic, meio- and macrofaunal organisms.

CO<sub>2</sub> was continuously added to the water column starting on day 0 in three fluxes so that that pH levels of the water column stabilised around 8.0, 7.5 and 6.8 respectively (Figure 1), corresponding to CO<sub>2</sub> pressure of 0.8, 2.6 and 16 m-atm respectively (Table 1). In unexposed control conditions, pH was 8.3 and CO<sub>2</sub> pressure 0.4 m-atm.

15

Table 1 CO<sub>2</sub> fluxes to the test systems and the related CO<sub>2</sub> pressure and pH in the water column.

CO <sub>2</sub> flux (ml/min)	CO <sub>2</sub> pressure (m-atm)	pH (average)
0	0.4	8.3
3	0.8	8.0
15	2.6	7.5
75	16	6.8

Bivalve molluscs and algae are important groups of fouling organisms. Figure 2 depicts the impact of increased CO<sub>2</sub> levels on reproduction of mollusks. As representative of bivalve molluscs, the cockle *Cerastoderma edule* was included in the experimental ecosystems. Although it was clear that shells became less robust at higher CO<sub>2</sub> levels, the adults survived all treatments. Reproductive success, however, was strongly affected. At 2.6 m-atm CO<sub>2</sub> and higher, reproduction was almost completely inhibited (Figure 2). The poor condition of the adult shells indicates erosion of the shell carbonates. The adults can withstand this situation as long as the shell maintains its protective function. It

25

is likely that under these conditions it is not possible for mollusc larvae to develop the shell that is essential for further development and survival. The impact of the elevated CO<sub>2</sub> for fouling prevention concerning the reproductions of bivalve molluscs and the sessile algae is clear at different endpoints.

5

The impact of increased CO<sub>2</sub> levels on sessile algae is depicted in Figure 3.

Roughly speaking algae can appear planktonic, suspended in the water column, or sessile, on sediments and substrates. By definition, only the sessile algae are concerned for fouling. Although CO<sub>2</sub> serves as a fertiliser for planktonic algae, 10 our study revealed an opposite effect on sessile algae (Figure 3). The dataset shows a 50% reduction of the algal biomass at 2.6 m-atm CO<sub>2</sub> and over 90% reduction at 16 m-atm CO<sub>2</sub>. The mechanism behind this is not understood yet, but the experimental set-up excludes competition with planktonic algae as the cause.

15

### Conclusion

These results indicate that a CO<sub>2</sub> pressure of 1.6 m-atm (resulting in this seawater in a pH of 6.8) is sufficient to prevent the settlement of cockle larvae and to reduce development of sessile algae with 90%. This makes that CO<sub>2</sub> has 20 the potential to be used to prevent fouling of marine organisms. Although sensitivity of other species still has to be tested, it is likely that similar results will be found with fresh water species.

## Claims

1. A method of reducing and/or preventing fouling on a surface of a component that is in contact with water, the method comprising: transferring  
5 carbon dioxide to the water to bring the water at a pH of at most 7.5, whereby the water is not pressurized.
2. The method according to claim 1, wherein the water is sea water.
- 10 3. The method according to claim 2, whereby the amount of carbon dioxide that is transferred to the sea water is at least 10 mg CO<sub>2</sub>/L.
4. The method according to any one of the previous claims, whereby the water is for cooling of an industrial plant, for example a power plant.
- 15 5. The method according to any one of the previous claims, whereby the carbon dioxide is produced by a plant that is cooled with the water.
6. The method according to any one of the previous claims, whereby the water  
20 is filtered prior to transferring carbon dioxide to the water.
7. The method according to any one of the previous claims, whereby the carbon dioxide is filtered prior to transferring the carbon dioxide to the water.
- 25 8. Cooling system comprising means for transferring carbon dioxide to the cooling water to bring the cooling water at a pH of at most 7.5, whereby the cooling water is not pressurized.
9. Cooling system according to claim 8, for cooling of an industrial plant, for  
30 example a power plant.

10. Cooling system according to claim 8 or claim 9, wherein the cooling water is sea water.
11. Cooling system according to any one of claims 8-10, which is a once-  
5 through system.
12. Cooling system according to any one of claims 8-10, which is a recirculating system.
- 10 13. Cooling system according to any one of claims 8-11, wherein the cooling water is cooled prior to discharging the cooling water.
14. Cooling system according to claim 12, wherein the cooling water is cooled prior to its reuse as cooling water.  
15
15. Industrial plant, comprising a cooling system according to any one of claims 8-14.

Figure 1

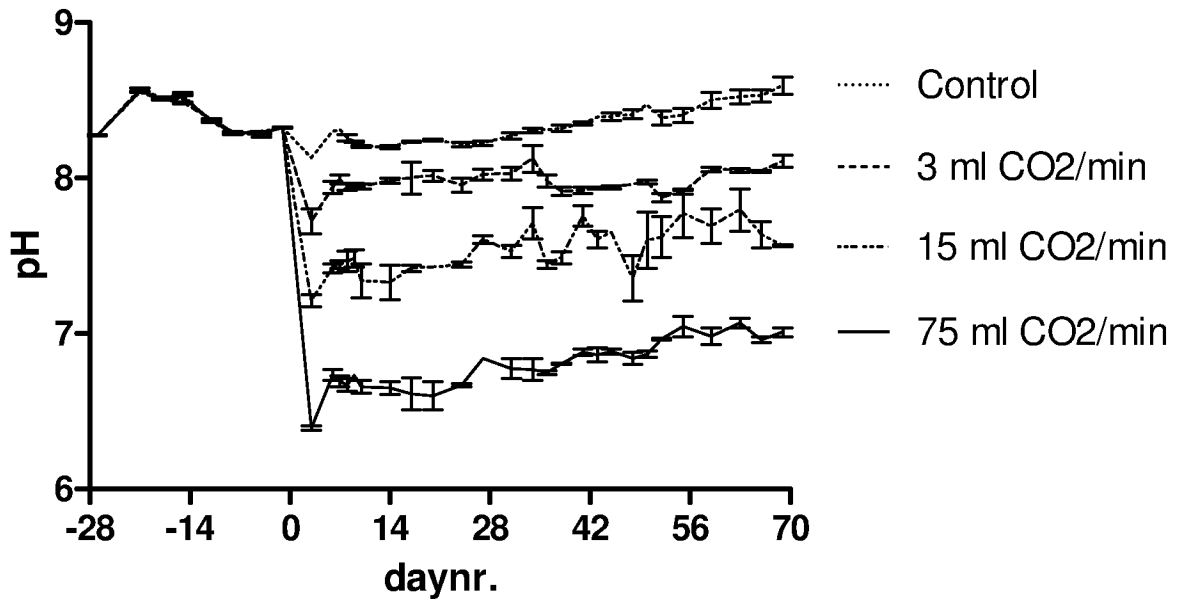


Figure 2

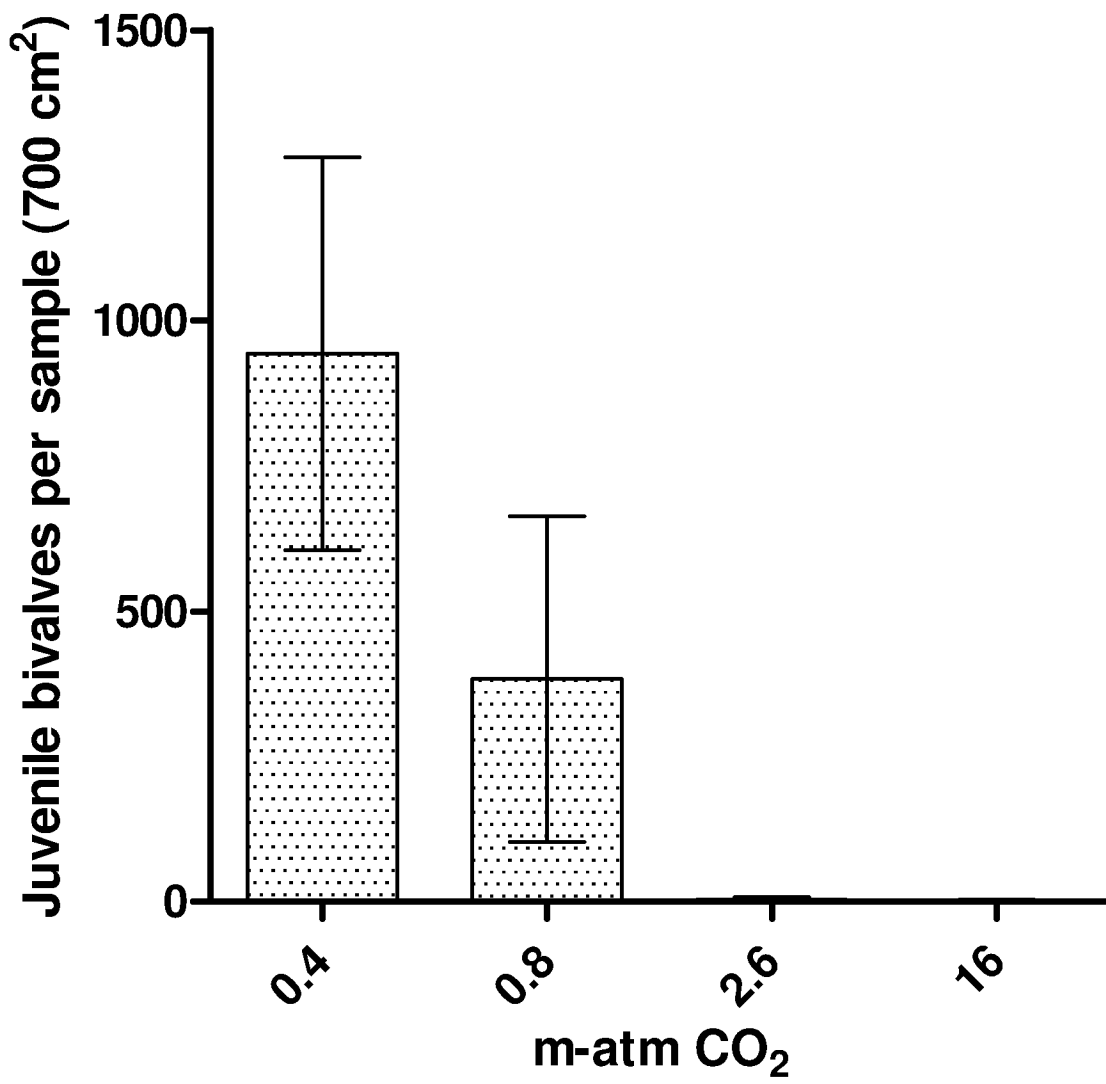
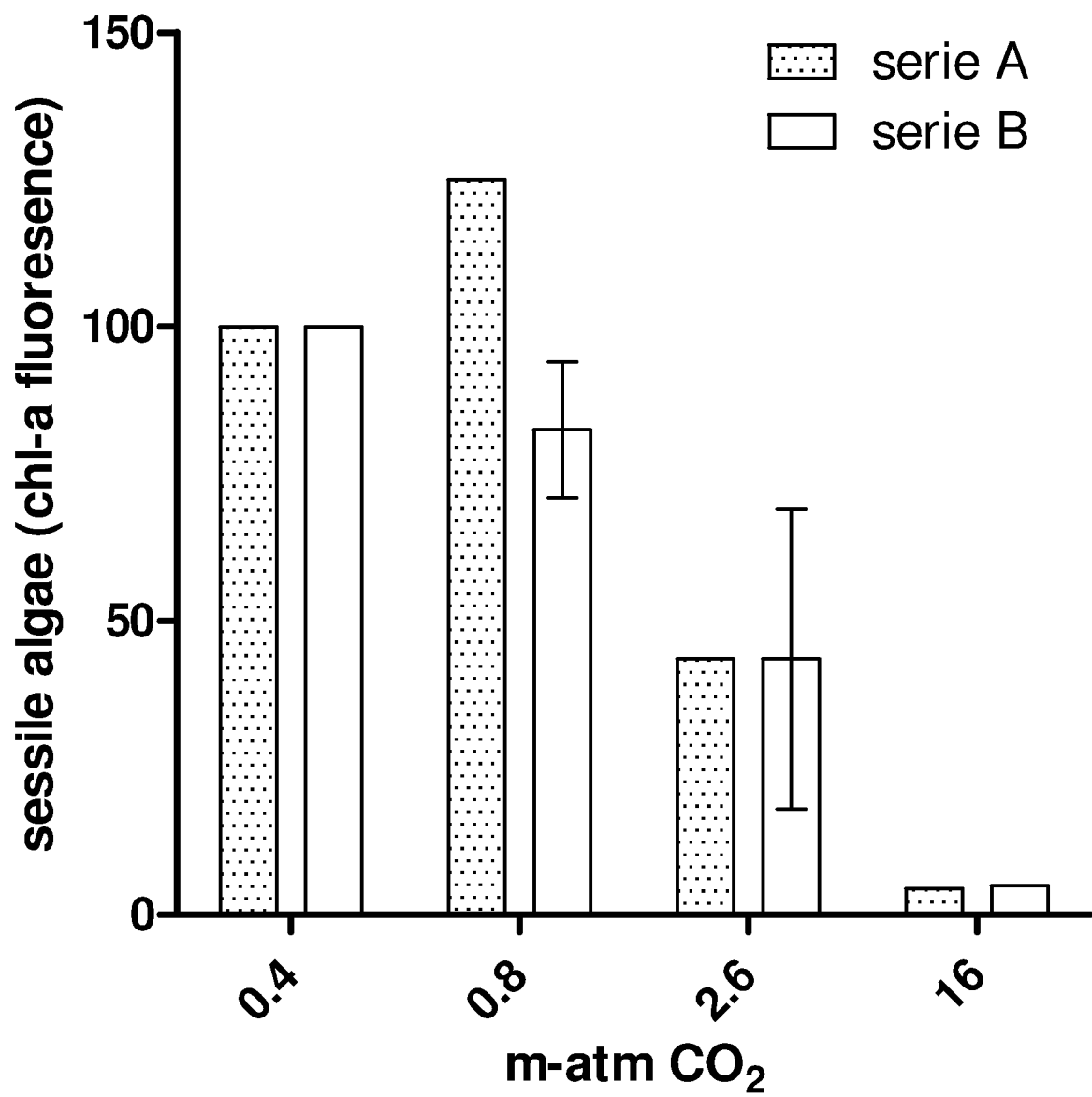


Figure 3





# INTERNATIONAL SEARCH REPORT

International application No PCT/NL2014/050341
---

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C02F1/66  
ADD. C02F103/02

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)  
C02F

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	FR 2 801 300 A1 (CARBOXYQUE FRANCAISE [FR]) 25 May 2001 (2001-05-25)	1,8,15
Y	claims 1-3; figures 1-3 -----	1-15
X	FR 2 832 143 A1 (JEVANOFF ANDRE [FR]) 16 May 2003 (2003-05-16)	1
	page 5, line 4 - page 5, line 11; claims 1-3,5-7; figure 1 -----	
X	US 4 547 294 A (GOELDNER RICHARD W [US]) 15 October 1985 (1985-10-15)	1,8,15
Y	claims 1,3-10; table 1 -----	1-15
X	EP 0 451 434 A1 (DENAC NV [BE]) 16 October 1991 (1991-10-16)	1,8,15
Y	claims 1,3,4,12; tables 1,2 -----	1-15
	-/--	

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

22 July 2014

Date of mailing of the international search report

04/08/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Van Iddekinge, R

**INTERNATIONAL SEARCH REPORT**

International application No PCT/NL2014/050341
---

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP H07 109585 A (KURITA WATER IND LTD; SUMITOMO METAL IND) 25 April 1995 (1995-04-25)	1, 8, 15
Y	paragraphs [0002], [0007], [0011] -----	1-15
X	US 5 424 032 A (CHRISTENSEN RONALD J [US] ET AL) 13 June 1995 (1995-06-13)	1, 8, 15
Y	column 3, line 1 - column 3, line 6; claims 1,5-7; figures 1,2 -----	1-15
X	US 5 591 349 A (IKEDA AKIRA [JP] ET AL) 7 January 1997 (1997-01-07)	1
	column 3, line 37 - column 3, line 47; claims 1-6 -----	
Y	US 2010/032030 A1 (PETERSON ROBERT RAYMOND [US]) 11 February 2010 (2010-02-11)	1-15
	paragraphs [0004], [0009], [0067], [0090] -----	
X	US 6 821 442 B1 (WATTEN BARNABY JUDE [US]) 23 November 2004 (2004-11-23)	1, 8, 15
Y	cited in the application claims 1-18 -----	1-15

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/NL2014/050341
---

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2801300	A1	25-05-2001	CA 2360517 A1 31-05-2001 EP 1152985 A1 14-11-2001 FR 2801300 A1 25-05-2001 WO 0138237 A1 31-05-2001
-----			
FR 2832143	A1	16-05-2003	NONE
-----			
US 4547294	A	15-10-1985	NONE
-----			
EP 0451434	A1	16-10-1991	AT 109434 T 15-08-1994 AU 633718 B2 04-02-1993 DE 69011316 D1 08-09-1994 DE 69011316 T2 16-02-1995 DK 0451434 T3 05-12-1994 EP 0451434 A1 16-10-1991 ES 2061003 T3 01-12-1994 NZ 237800 A 29-01-1992 PT 97364 A 31-12-1991 ZA 9102696 A 24-12-1991
-----			
JP H07109585	A	25-04-1995	NONE
-----			
US 5424032	A	13-06-1995	AT 153319 T 15-06-1997 BR 9306779 A 08-12-1998 CA 2139934 A1 03-02-1994 DE 651730 T1 14-03-1996 DE 69310912 D1 26-06-1997 DE 69310912 T2 16-10-1997 EP 0651730 A1 10-05-1995 ES 2076133 T1 01-11-1995 US 5424032 A 13-06-1995 WO 9402423 A1 03-02-1994
-----			
US 5591349	A	07-01-1997	DE 69305411 D1 21-11-1996 DE 69305411 T2 15-05-1997 EP 0567860 A1 03-11-1993 US 5591349 A 07-01-1997
-----			
US 2010032030	A1	11-02-2010	NONE
-----			
US 6821442	B1	23-11-2004	NONE
-----			