



(51) International Patent Classification:

**C02F 5/10** (2006.01)      **D21H 23/08** (2006.01)  
**C23F 14/02** (2006.01)      **D21H 23/20** (2006.01)  
**D21F 7/06** (2006.01)      **G01N 37/00** (2006.01)

(21) International Application Number:

PCT/CA2010/001205

(22) International Filing Date:

4 August 2010 (04.08.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/235,699      21 August 2009 (21.08.2009)      US  
12/781,827      18 May 2010 (18.05.2010)      US

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(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, 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, IS, JP, KE, KG, KM, 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, PE, PG, PH, PL, PT, RO, RS, RU, 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, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

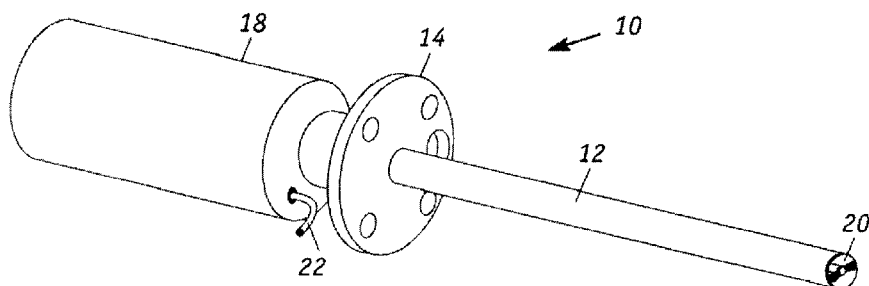
**Declarations under Rule 4.17:**

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

**Published:**

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

(54) Title: LIQUID COMPOSITION SENSOR IN SCALING ENVIRONMENT



**FIG. 1**

(57) **Abstract:** Scale formation on the electrode(s) of a liquor sensor can be prevented by continuously delivering a water-soluble scale inhibitor or dispersant into the vicinity of the electrodes of a liquor sensor device. Scale inhibitors include, for instance, polymers that are derived from acrylic acid, maleic acid, acrylamide acid, phosphonate, and combinations thereof. An aqueous mixture of scaling inhibitor continuously delivered to the probe tip of the liquor sensor that was placed in a kraft pulping liquor allowed the sensor to operate accurately for over a month without having to be cleaned of scale.

## **Liquid Composition Sensor in Scaling Environment**

### **REFERENCE TO RELATED APPLICATIONS**

**[0001]** This application claims priority to U.S. Provisional Application 61/235,699 that was filed on August 21, 2009.

### **FIELD OF THE INVENTION**

**[0002]** The present invention generally relates to methods for inhibiting scale formation in aqueous alkaline systems of chemical pulping processes and particularly to techniques for inhibiting formation, deposition and adherence of calcium salt scale deposits on the electrodes of composition measuring sensors.

### **BACKGROUND OF THE INVENTION**

**[0003]** Pulp making is carried out on large industrial scales worldwide to produce paper. Accordingly it is highly desirable that such pulp making operations be carried out in a cost effective, efficient operation with minimum manufacturing equipment downtime and minimum periods of reduced pulp making process equipment efficiency.

**[0004]** The basic steps in industrial pulp making are to convert plant fiber into chips, convert chips into pulp, wash the pulp, (optionally) bleach the pulp, and transform the pulp into suitable paper which can be used in a variety of paper products.

**[0005]** Typically, several chemical pulping processes are used in industrial pulp making operations. Well known industrial alkaline chemical pulping processes include the Kraft (or sulfate), soda and alkaline sulfite processes. The Kraft process makes the strongest fibers of any pulp producing process and is the most commonly used pulp making process in part due to its efficient recovery process for the cooking chemicals. While the present invention has applicability to any of the above alkaline chemical pulping processes, it is particularly useful with the Kraft process.

**[0006]** In the Kraft process, wood chips are digested to dissolve the lignin that holds the wood fibers together thereby producing clean fibers for further processing into a myriad of paper-based products. The digestion of the wood chips occurs in an alkaline solution mainly consisting of sodium hydroxide and sodium sulfide. As the process

proceeds, the hydroxide becomes consumed and the sulfide slowly converts to hydroxide. The resulting pulp fibers are washed and removed leaving a solution, called black liquor, containing the lignin dissolved from the wood chips and residual hydroxide and sulfide. The black liquor is burned in a recovery boiler leaving a smelt primarily consisting of sulfide and sodium carbonate. This smelt is dissolved in water or "weak wash liquor" to produce green liquor. The objective of the remaining steps of the process is to convert sodium carbonate in the green liquor to sodium hydroxide so that the sodium hydroxide can be recycled and reused in the digesting process.

**[0007]** The reaction for converting the sodium carbonate to sodium hydroxide is often referred to as the "causticizing" process or reaction and is carried out in a "slaker" and a series of "causticizers," to produce a white liquor that ideally has a high degree of sodium hydroxide and only a small amount of sodium carbonate. The causticizing reaction is controlled by the amount of lime (calcium oxide) introduced to the slaker and the flow rate of green liquor into the slaker. To produce white liquor having the appropriate characteristics, the flow rate of lime into the slaker is carefully regulated. It is essential to measure the characteristics of the green liquor and/or the white liquor in order to control the causticizing reaction.

**[0008]** Various types of sensor devices have been used to monitor and control the composition of green and white liquor. For example, the sensor device can comprise a series of electrodes embedded in housing mounted inside a digester or recausticizing tank. Unfortunately, calcium scales develop rapidly on the electrodes in such hostile environments resulting in measurement drift and loss of accuracy. The sensor devices must be physically cleaned to remove the scales. US Pat. No. 6,235,123 to Millar describes a sensor device in which the electrodes are embedded in the surface of a housing that is equipped with a cleaning baffle. When cleaning is required, the cleaning baffle is rotated from a first position adjacent the electrodes, where the baffle does not interfere with contact between the liquor and the electrodes, to a second position, so that the baffle covers the electrodes from the liquor. Thereafter, a cleaning solvent is directed under pressure to the electrodes through a solvent channel. The spraying action is said to remove built-up materials on the electrodes. This in-situ cleaning technique has proven not to be effective in hostile environments in part because during the frequent cleaning

cycles, the position of the baffles over the electrodes result in significant down times where the sensor device is not operating.

#### SUMMARY OF THE INVENTION

**[0009]** The present invention is based in part on the demonstration that scale formation on the electrode(s) of a liquor sensor can be drastically reduced by continuously delivering a water-soluble scale inhibitor or dispersant into the vicinity of the electrodes of a liquor sensor device. Preferred scale inhibitors are suitable polymers that include, for example, acrylic acid polymer, maleic acid polymer, acrylamide acid polymer, phosphonate polymer, and combinations thereof. The presence of the scale inhibitor does not interfere with the measurements by the liquor sensor. Multi-electrode composition measuring devices employing the inventive technique are able to continuously function accurately for over a month period without having to be removed from the liquor and physically cleaned. Without the water-soluble scale inhibitor, the same measuring devices must be cleaned every few days.

**[0010]** In one aspect, the invention is directed to a system for measuring at least one component that includes NaOH, Na<sub>2</sub>S, and Na<sub>2</sub>CO<sub>3</sub> in a kraft pulping liquor that has a pH of at least 8.5 that includes:

**[0011]** a sensor device having at least one electrode that is configured to be positioned in the pulping liquor;

**[0012]** a source of an aqueous mixture of scaling inhibitors; and

**[0013]** means for continuously distributing an effective amount of the aqueous mixture of scaling inhibitors into the pulping liquor in the vicinity of the at least one electrode, characterized in that scale deposition in the form of calcium salts that are present in the pulping liquor onto the at least one electrode is effectively controlled to permit continuous operation of the sensor device for more than a month without cleaning.

**[0014]** In another aspect, the invention is directed to a method of inhibiting the formation of scale on an electrode of a pulp liquor sensor device that measures at least one component that includes NaOH, Na<sub>2</sub>S, and Na<sub>2</sub>CO<sub>3</sub> in a kraft pulp liquor that includes the steps of:

- [0015]** immersing the electrode of the sensor device into a kraft pulp liquor that has a pH of at least 8.5;
- [0016]** providing a source of an aqueous mixture of scaling inhibitors; and
- [0017]** continuously distributing an effective amount of the aqueous mixture of scaling inhibitors into the kraft pulp liquor in the vicinity of the electrode characterized in that scale deposition in the form of calcium salts that are present in the pulping liquor onto the electrode is effectively controlled to permit continuous operation of the sensor device for more than a month without cleaning.

#### BRIEF DESCRIPTION OF THE DRAWINGS

- [0018]** Figure 1 illustrates a liquor sensor for measuring the composition of pulping liquors;
- [0019]** Figure 2 is an enlarged view of the probe tip; and
- [0020]** Figure 3 illustrates a system for measuring the composition of pulping liquors that is equipped with a continuous source of scale inhibitors.

#### DETAIL DESCRIPTION OF PREFERRED EMBODIMENTS

**[0021]** As shown in Fig. 1, the liquor sensor apparatus 10 comprises a multi-electrode composition measuring device that includes a probe tip assembly 12, mounting bracket 14, and rear assembly 18. The sensor apparatus is particularly suited for measuring the concentrations of NaOH, Na<sub>2</sub>S, Na<sub>2</sub>CO<sub>3</sub> and/or other active chemicals that are present in liquor composition. A suitable multi-electrode unit is described in US Pat. No. 6,416,651 to Millar, which is incorporated herein by reference. Probe tip assembly 12, which is typically 1-2 meters in length, positions the probe tip 20 a short distance into a process vessel of the pulping process so as to be in contact with the liquor to be measured. Rear assembly 18 can include a reservoir that contains an aqueous mixture of a scaling inhibitor. The height of the reservoir within the rear assembly, relative to the probe tip 20, allows the scaling inhibitor to pass into the liquor by gravity; however, where necessary, pumps can be employed to regulate the flow rate into the liquor. Wires 22 connect probe tip 20 to a computer (not shown).

**[0022]** Figure 2 shows probe tip 20 configured with the external surfaces of electrodes 26, 28 and 30 being substantially flush with surface 32 of housing 34. The electrodes are preferably located on one side of housing 34 and on the opposite side is aperture 36 through which a mixture of scaling inhibitors exits. The contour of vertical wall 38 that projects from housing 34 is configured to flank the electrodes. In this fashion, the aqueous mixture of scaling inhibitors exiting aperture 36 will be directed toward the electrodes. The exterior components of liquor sensor apparatus 10 are preferably made of corrosion resistant metal such as, for example, stainless steel. Similarly, the electrode tips that are exposed in the liquor composition are preferably made of platinum.

**[0023]** As shown in Figure 3, rear assembly 18 is connected to a source of scaling inhibitor 2. A pump 4 that is regulated by a controller (not shown) delivers the scale inhibitor mixture to the rear assembly 18. The mixture then flows through probe tip assembly 12 and into the liquid in the vicinity of the electrodes at the probe tip 20 (Fig. 2). A continuous stream of the mixture is metered out from probe tip 20 that is immersed in the liquor. With the present invention, it is not necessary to apply the scale inhibitor mixture under pressure directly onto the electrode surfaces. Moreover, the electrodes are not shielded nor covered with any baffle from the liquor during any cleaning phase, in other words, the electrodes operate continuously and there is no downtime of the composition-measuring device. The present invention is particularly suited for measuring the compositions in the white liquor and green liquor in the kraft process, which is further described, for instance, in US Pat. Application Publication 2009/0255829 to Tixier et al. and US Pat. No. 5,822,220 to Baines, which are both incorporated by reference.

**[0024]** Suitable scaling inhibitors prevent scale from depositing onto the electrodes and other surfaces of the probe tip. The types of scale that can be prevented from being deposited include, for example, calcium carbonate ( $\text{CaCO}_3$ ) and personite ( $\text{Ca}_x\text{Na}_y\text{CO}_3$ ). Preferred scale inhibitors are suitable polymers include, for instance, acrylic acid polymer, maleic acid polymer, acrylamide acid polymer, phosphonate polymer and combinations thereof. Chemicals for use as scaling inhibitors are commercially available, for instance, from Kemira Oyj (Finland). A preferred source is

FENNODISPO 5300 from Kemira, which is an aqueous acrylic polymer. Active ingredients sold under the BELCLEN line of products from BWA Water Additives UK Limited (UK) are also suitable. For example, BELCLEN 200, which has maleic homopolymers, BELCLEN 283, which has maleic terpolymers, and BELCLEN 110, which has carboxylic acid based polymers, can be employed.

**[0025]** Suitable scaling inhibitors are typically prepared by diluting the chemicals with sufficient amounts of water to form aqueous mixtures containing about 1 to 10% active components. In use, the mixture is continuously metered through the aperture in the probe tip at a flow rate of from 1 ml/min to approximately 5 to 10 ml/min to generate 1 to 50 ppm of actives in the vicinity of the electrodes of the probe tip.

**[0026]** It has been demonstrated that scaling will adversely affect the accuracy of a liquor sensor after just one day of measurement in a hostile pulp liquor environment. However, when an aqueous mixture of scaling inhibitor formulated from FENNODISPO 5300 was employed and continuously delivered to the probe tip of the liquor sensor, the sensor operated accurately for over a month without having to be cleaned of scale.

**[0027]** The foregoing has described the principles, preferred embodiment and modes of operation of the present invention. However, the invention should not be construed as limited to the particular embodiments discussed. Instead, the above-described embodiments should be regarded as illustrative rather than restrictive, and it should be appreciated that variations may be made in those embodiments by workers skilled in the art without departing from the scope of present invention as defined by the following claims.

What is claimed is:

1. A system for measuring a component in a liquid that comprises:  
a sensor device (10) that is configured to be positioned in the liquid;  
a source of an aqueous mixture of scaling inhibitors (2); and  
5 means for continuously distributing (4, 18) an effective amount of the aqueous mixture of scaling inhibitors into the liquid in the vicinity of the sensor device (10),  
characterized in that scale deposition in the form of salts that are present in the liquid  
onto the sensor device (10) is effectively controlled to permit continuous operation of  
the sensor device for more than a month without cleaning.  
10
2. The system of claim 1 wherein the scaling inhibitors are polymers selected  
from the group consisting of acrylic acid polymers, maleic acid polymers, acrylamide  
acid polymers, phosphonate polymers or mixtures thereof.
- 15 3. The system of claim 1 wherein the scaling inhibitors comprise a mixture of  
polymers that are derived from acrylic acid and maleic acid.
4. The system of claim 1 wherein the sensor device (10) has at least one  
electrode (26,28, 30) that is configured to be positioned in the liquid.  
20
5. The system of claim 4 wherein the aqueous mixture of scaling inhibitors is not  
applied directly onto the at least one electrode.
6. A method of inhibiting the formation of scale on an electrode that comprises  
25 the steps of:  
immersing the electrode (26, 28, 30) of a sensor device (10) into a liquid being  
measured;  
providing a source of an aqueous mixture of scaling inhibitors (2); and  
continuously distributing an effective amount of the aqueous mixture of  
30 scaling inhibitors into the liquid in the vicinity of the electrode (26,28, 30)  
characterized in that scale deposition in the form of salts that are present in the liquid

onto the electrode (26, 28, 30) is effectively controlled to permit continuous operation of the sensor device (10) for more than a month without cleaning.

7. The method of claim 6 wherein sufficient amounts of the aqueous mixture of active scaling inhibitors are released into the vicinity of the electrode to maintain a concentration of at least 1 ppm actives.

8. The method of claim 6 wherein the aqueous mixture of scaling inhibitors is not applied directly onto the one electrode (26, 28, 30).

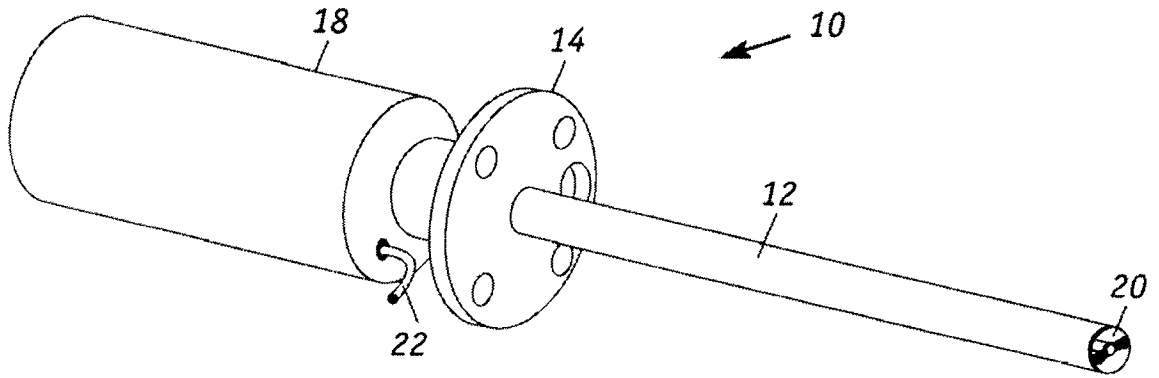
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9. The method of claim 6 wherein the liquid comprises a pulp liquor and the sensor device measures at least one component that includes NaOH, Na<sub>2</sub>S, and/or Na<sub>2</sub>CO<sub>3</sub> in a kraft pulp liquor that has a pH of at least 8.5.

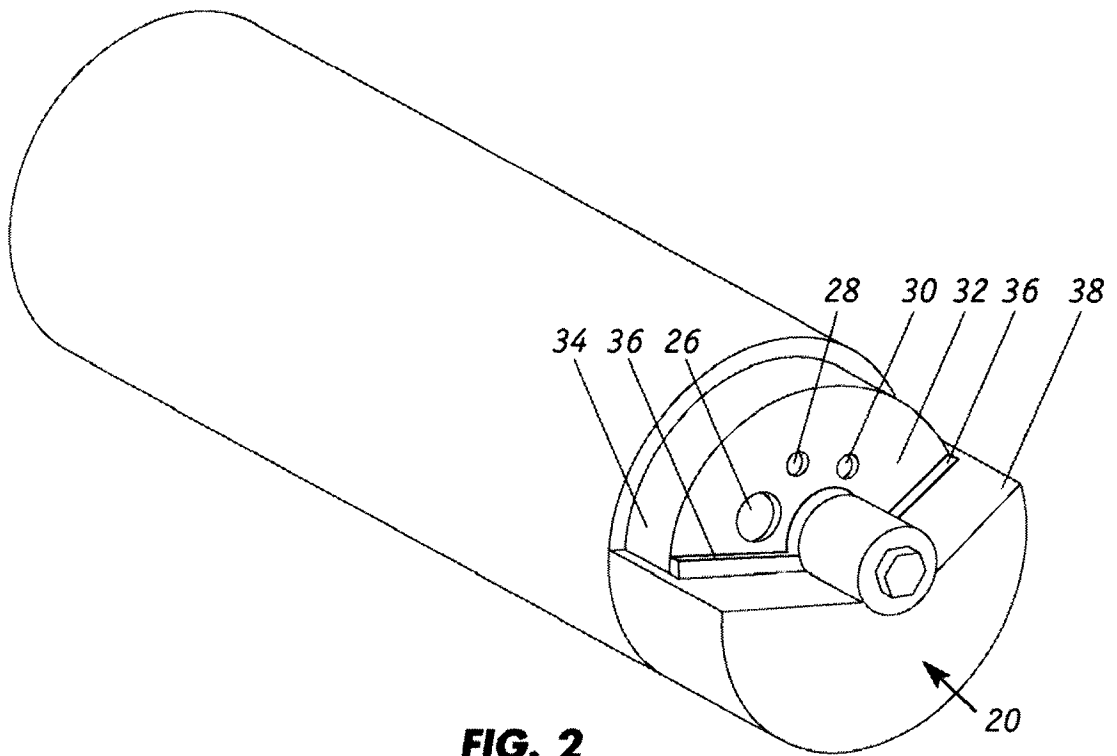
15 10. The method of claim 6 wherein sensor device (10) comprises the plurality of electrodes (26, 28, 30) that are mounted within a housing (34) and an effective amount of the scaling inhibitors is released into the pulping liquor toward the vicinity of the plurality of electrodes (26, 28, 30).

20 11. The method of claim 6 wherein the scaling inhibitors are polymers selected from the group consisting of acrylic acid polymers, maleic acid polymers, acrylamide acid polymers, phosphonate polymers or mixtures thereof.

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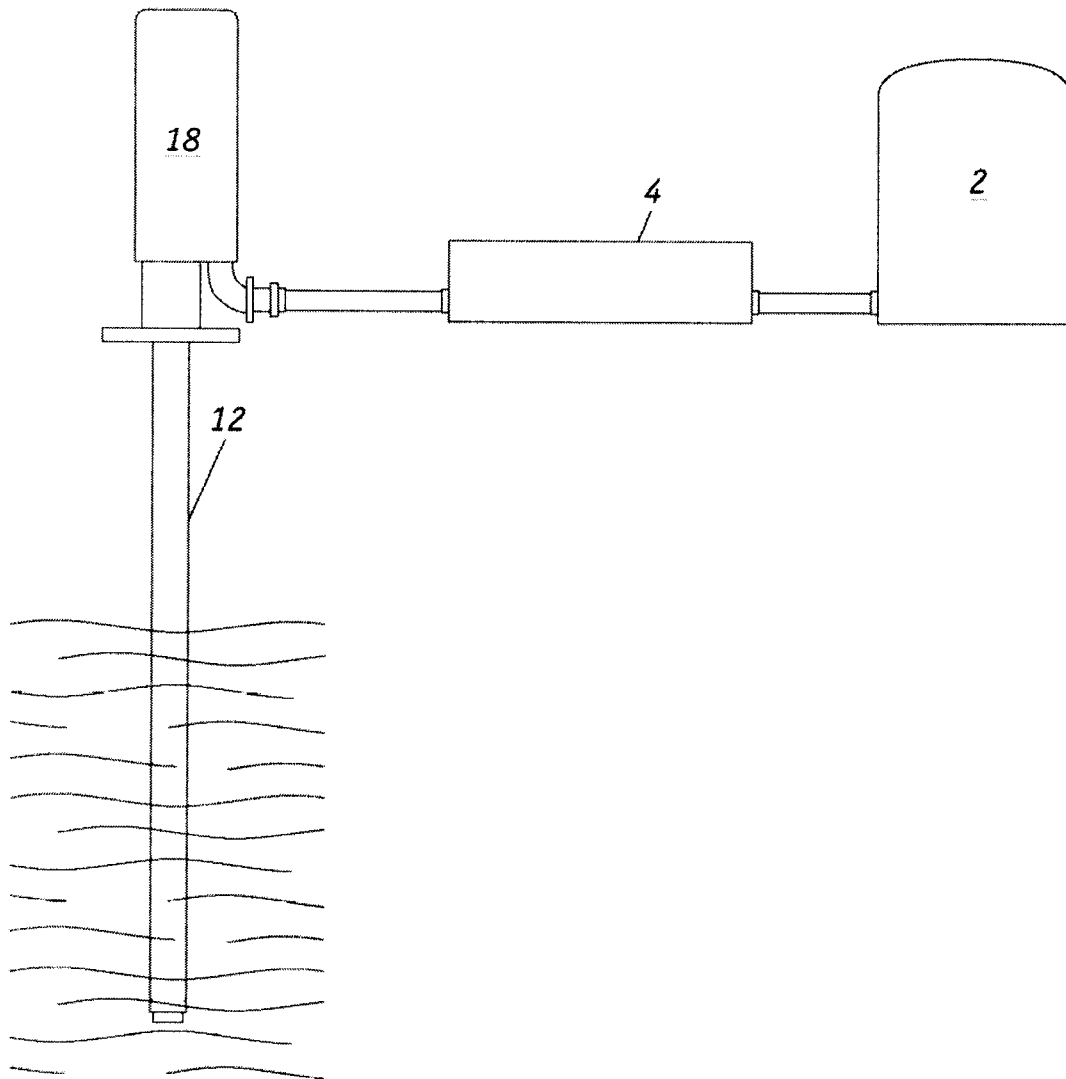


**FIG. 1**



**FIG. 2**

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**FIG. 3**

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/CA2010/001205

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC: <i>C02F 5/10</i> (2006.01) , <i>C23F 14/02</i> (2006.01) , <i>D21F 7/06</i> (2006.01) , <i>D21H 23/08</i> (2006.01) , <i>D21H 23/20</i> (2006.01) , <i>G01N 37/00</i> (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC: <i>C02F 5/10</i> (2006.01) , <i>C23F 14/02</i> (2006.01) , <i>D21F 7/06</i> (2006.01) , <i>D21H 23/08</i> (2006.01) , <i>D21H 23/20</i> (2006.01) , <i>G01N 37/00</i> (2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) TotalPatent, Canadian Patent Database, Esp@cenet Keywords: sensor, meter, probe, electrode, scale, inhibit, calcium carbonate		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 235 123 (Millar) 22 May 2001 (22-05-2001) the whole document	1, 4, 6, 10
A	US 6 416 651 (Millar) 9 July 2002 (09-07-2002) Figure 1 column 5, lines 54-67	1, 4, 6, 10
A	JP 2001 228 110 (Taguchi et al.) 24 August 2001 (24-08-2001) abstract	1, 4, 6, 10
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :	"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	
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"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
15 October 2010 (15-10-2010)	15 November 2010 (15-11-2010)	
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer  Charles Greenough (819) 994-0243	

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/CA2010/001205**

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US6235123B1	22 May 2001 (22-05-2001)	CA2331126A1 CA2331126C DE69913335D1 DE69913335T2 EP1076817A1 EP1076817B1 JP2002513931T WO9957551A1	11 November 1999 (11-11-1999) 30 June 2009 (30-06-2009) 15 January 2004 (15-01-2004) 30 December 2004 (30-12-2004) 21 February 2001 (21-02-2001) 03 December 2003 (03-12-2003) 14 May 2002 (14-05-2002) 11 November 1999 (11-11-1999)
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JP2001228110	24 August 2001 (24-08-2001)	NONE	