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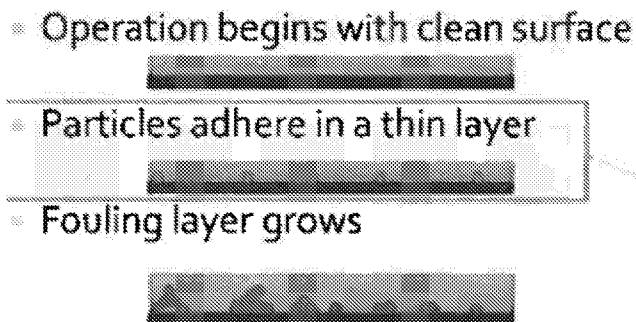


Figure 1

(57) Abstract: In general, the present invention is directed to materials that when in use resist fouling on their surfaces. Such materials may be used in the construction of various process equipment having surfaces exposed to a given fluid that contains a foulant or chemical substance that may deposit on, or adhere to, the surface and thereafter continue to grow on the surface resulting in deteriorated performance of the equipment and process. The materials are specifically selected using a method that takes into account the dielectric spectra of the fluid to which the surface is exposed and the surface itself. It has been unexpectedly found that if the dielectric spectra of the surface and the fluid are matched to within relative agreement, there should be no adhesion of the foulant on the surface. In some embodiments, the dielectric spectra to be matched include the intrinsic indexes of refraction.



## MATERIALS THAT RESIST FOULING AND METHODS FOR IDENTIFYING SAME

## BACKGROUND OF THE INVENTION

## Field of the Invention

5 [0001] The present invention is directed to methods for the reduction or elimination of fouling on material or component surfaces. More specifically, the present invention is directed to methods for the identification of materials of construction for such surfaces, either as coatings or as the materials themselves, having a dielectric spectrum that matches or is similar to that of the fluid to which the surface is exposed.

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## Description of Related Art

[0002] Fouling of a surface, or the undesired deposition of materials onto a given surface, is a problem that affects fields ranging from energy to transportation to medicine. Energy production and distribution systems are particularly susceptible to the detriments associated with fouling, as they rely on the continued cleanliness of their functional surfaces, for example, to transfer heat, catalyze chemical reactions, and resist corrosion. Particulate fouling, or the adhesion of particulates to surfaces, is present to some extent in almost all geothermal plants, oil refineries, nuclear plants, chemical processing, and marine systems. Fouling of internal pipe surfaces increases pressure drops across components, reduces heat transfer efficiency, and may block coolant channels entirely, resulting in loss of process efficiency and possibly necessitating the replacement of components. Considering the costs of increased energy consumption, reduced throughput, and maintenance associated with fouling gives an estimated economic impact of billions of dollars, estimated to cost the U.S. \$15 billion in 2013 alone.

25 [0003] Teflon or other slippery polymers may be used in some situations to reduce or minimize fouling, as they resist the buildup of almost all potential foulants. However, many energy systems where fouling occurs operate in conditions too harsh for Teflon or any organic material to remain stable. Therefore, a more general solution to the problem of fouling is needed. Specifically, a solution to fouling in harsh environments, such as those in various energy systems, is needed.

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## BRIEF SUMMARY OF THE INVENTION

[0004] Initial fouling or initial deposition of a foulant on a surface can be caused by van der Waals forces, often the main force determining the adhesion of foulants in energy

systems. Therefore, preventing such forces should reduce or eliminate any initial deposition of the foulant caused by van der Waals forces, which, in turn, would result in reduced fouling or in the elimination of fouling. The theory of van der Waals forces shows that by obtaining or engineering a close match between the dielectric spectra of either the surface being fouled or of the foulant with that of the fluid would lead to the significant reduction or elimination of van der Waals forces. Of course, for a given system, the potential foulant and the fluid are essentially fixed or determined by the system and may not be capable of variation. In other words, the compositions of the foulant and the fluid may not be changed simply to prevent fouling without sacrificing the main objective of the system in the first place. Therefore, by selecting a material of construction for the surface exposed to potential fouling, either as a coating or as the material itself, with a dielectric spectrum that matches or approximates that of the fluid to which it is exposed should reduce or eliminate van der Waal forces such that deposition of the foulant is prevented.

**[0005]** In one embodiment, the present invention provides a method for selecting a material of construction for a surface exposed to a fluid having a foulant, comprising selecting a material of construction for a surface exposed, during use, to a fluid comprising a foulant, wherein the material of construction, either a coating on the material or the material itself, whichever is exposed to the fluid, has an index of refraction within the full refractive index spectrum that matches or approximates an index of refraction within the full refractive index spectrum of the fluid.

**[0006]** In one embodiment, the present invention provides a method for selecting a material of construction for a surface exposed to a fluid having a foulant, comprising selecting a material of construction for a surface exposed, during use, to a fluid comprising a foulant, wherein the material of construction has an index of refraction within the full refractive index spectrum that is within 20% of an index of refraction within the full refractive index spectrum of the fluid. It should be appreciated that in one embodiment, at least one value within the complete spectrum needs to match within 20%.

**[0007]** In another embodiment, the present invention provides a method for selecting a material of construction for a surface exposed to a fluid having a foulant, comprising selecting a coating for a surface exposed, during use, to a fluid comprising a foulant, wherein the coating has an index of refraction within the full refractive index spectrum that is within 20% of an index of refraction within the full refractive index spectrum of the fluid.

**[0008]** In another embodiment, the present invention provides a material of construction, comprising a body having a surface that is exposed to a fluid comprising a

foulant during use; and an index of refraction within the full refractive index spectrum that is within 20% of an index of refraction within the full refractive index spectrum of the fluid.

[0010] In another embodiment, the present invention provides a coating for a surface, comprising a coating for a surface that is exposed to a fluid comprising a foulant during use; and an index of refraction within the full refractive index spectrum that is within 20% of an index of refraction within the full refractive index spectrum of the fluid. In one embodiment, the coating is disposed on the surface of the material.

#### BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

10 [0011] Figure 1 illustrates the fouling process beginning with a clean surface, then attachment of a monolayer of particles, followed by continued scale growth;

[0012] Figure 2 illustrates a diagram of EELS, along with typical VEELS calculated and measured spectra;

15 [0013] Figure 3 shows the Hamaker constants of various materials using full-spectral and Tabor-Winterton calculations;

[0014] Figure 4 illustrates one example of a cantilever used to measure the force of adhesion using AFM-FS;

[0015] Figure 5 illustrates a vacuum-inert AFM chamber; and

[0016] Figure 6 schematically shows the use of the USPEX algorithm.

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#### DETAILED DESCRIPTION OF THE INVENTION

[0017] Various embodiments of the invention are described below in conjunction with the Figures. However, this description should not be viewed as limiting the scope of the present invention or as setting forth the only embodiments of the invention. Rather, it should be considered as exemplary of various embodiments of the invention since invention encompasses other embodiments not specifically recited in this description such as alternatives, modifications, and equivalents within the spirit and scope of the invention and as defined by the claims. Accordingly, it should be appreciated that references to “the invention” or “the present invention” should not be construed as meaning that the invention is directed to only one embodiment or that every embodiment must contain a given feature described in connection with another embodiment or described in connection with the use of such phrases.

30 [0018] In general, the present invention is directed to materials that in use resist fouling on their surfaces. Such materials may be used in the construction of various process

equipment having surfaces exposed to a given fluid that contains a foulant or chemical substance that may deposit on, or adhere to, the surface and thereafter continue to grow on the surface resulting in deteriorated performance of the equipment and/or the process. The materials are specifically selected using a method that takes into account the

5 dielectric/refractive spectra (which are directly related) of the fluid to which the surface is exposed. It has been unexpectedly found that if the dielectric spectra of the surface and the fluid are matched, or are close, there should be no adhesion of the foulant on the surface. In some embodiments, the dielectric spectra to be matched include the intrinsic index of refraction.

10 **[0019]** More specifically, and without being limited by theory, the initial deposition or adherence of a foulant, or foulant particles, on a surface is believed to be due to van der Waals forces between the surface and the foulant. Based upon the Lifshitz theory of van der Waals forces, it has been determined that if the dielectric spectrum of either the foulant or the surface material is the same as that of the fluid carrying the foulant and to which the surface  
15 is exposed, then there should be no van der Waals forces. By eliminating such forces, there should be no adherence of the foulant on the surface or no formation of an initial monolayer of foulant particles on the surface and, therefore, no continued growth of any foulant on the surface. Figure 1 illustrates the fouling process beginning with a clean surface, then attachment of a partial or complete monolayer of particles, followed by continued scale  
20 growth. The present invention focuses on reducing or eliminating the initial deposition of the monolayer of particles.

**[0020]** It should be appreciated that matching the dielectric spectrum of the foulant to the fluid will produce the same result; however, in most practical applications, neither the foulant nor the fluid can be “selected” since these are fixed by the process being used.  
25 Therefore, the only practical method would be to select the appropriate materials of construction for the surface exposed to the fluid. It should be appreciated that the materials of construction includes the material used for the surface exposed to the fluid and in some embodiments includes a coating on the underlying material used. Therefore, it should be appreciated that if a given surface is coated, the coating can be similarly selected based upon  
30 matching its dielectric spectrum to that of the fluid. It should also be appreciated that “matching” the dielectric spectra does not necessarily mean that the dielectric spectra of the surface and fluid must match exactly. In some embodiments, the “match” may be within  $\pm 0$ -20% of each other. In some embodiments, the “match” may be within  $\pm 5\%$ ,  $\pm 10\%$ , or  $\pm 20\%$ ,

and these “matches” may be wavelength- or frequency-dependent, tuned to the wavelength(s) or frequency(ies) that determine van der Waals forces most significantly.

[0021] Without being bound by theory, the following presents an analysis of the discovery that by matching dielectric spectra, a reduction or elimination of van der Waals (vdW) forces would occur. The vdW force between two materials  $a$  and  $b$  in a fluid  $f$  is of the inverse square form with separation  $r$ , similar to Coulomb interactions:

$$F_{afb}^{vdW} = -\frac{A_{afb}^{Ham}}{12\pi r^2} \quad (1)$$

10 [0022] The force is directly proportional to  $A_{afb}^{Ham}$ , known as the Hamaker constant. This constant defines the magnitude of the force and whether the force is attractive or repulsive (the latter being uncommon). Since the vdW force arises from coupled electron motion creating induced dipoles, the Hamaker constant is calculated by taking into account a material's response to oscillating electric fields—in other words, optical properties like the index of refraction or reflectivity. It is most direct to calculate the Hamaker constant from the material's imaginary-frequency dielectric response  $\epsilon(\zeta)$ , but this difficult-to-interpret quantity is directly related to more conventional measurements such as reflectivity or ellipsometry. It may also be obtained to high accuracy by more advanced measurements such as Valence Electron Energy Loss Spectroscopy (VEELS). The formula for a full-spectrum relativistic Hamaker constant (the formula with the fewest assumptions and limitations, but also the most complex) is:

$$A_{afb}^{Ham} = \frac{3}{2} k_B T \sum_{n=0}^{\infty} R_n(r) \Delta_{af}(\zeta_n) \Delta_{bf}(\zeta_n) \quad (2)$$

25 where  $k_B$  is Boltzmann's constant in  $\frac{eV}{K}$ ,  $T$  is the temperature in Kelvin,  $R_n(r)$  is an optical retardation factor (which accounts for differing path lengths for differently polarized photon propagation), and  $\Delta_{jk}$  is the difference in dielectric response to a *virtual photon* at an imaginary (complex) frequency  $\zeta_n - i\nu_n$ , where  $n$  is a discrete energy level from 0 to  $\infty$ . The  $\Delta_{jk}$  variables can be thought of as contributions to adhesion energy based on differing polarizability at different frequencies or differences in electron vibrations at different frequencies. Each of these can be expressed as follows:

$$\Delta_{jk}(\zeta) = \frac{\varepsilon_j(\zeta) - \varepsilon_k(\zeta)}{\varepsilon_j(\zeta) + \varepsilon_k(\zeta)} \quad (3)$$

here  $\varepsilon(\zeta)$  is the dielectric response function of material  $j$  at imaginary frequency  $\zeta$ . Finally, each of these can be expressed in terms of its real, measurable components by applying the  
 5 Kramers-Kronig (KK) relation, connecting the real and imaginary components of any causal function:

$$\varepsilon(\zeta) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega \varepsilon(\omega)}{\omega^2 + \zeta^2} d\omega \quad (4)$$

10 where  $\omega$  is a real frequency. In this way, we can transform tabulated optical data into a Hamaker constant, which can also be measured using atomic force microscope force spectroscopy (AFM-FS) via the adhesion force. Using this knowledge, we have one deterministic angle of attack: the difference term in Equation 3. If the two imaginary  
 15 dielectric spectra of any of the materials  $a$  and  $b$  with the fluid  $f$  are equal, then theoretically no adhesion should take place. Because the real and imaginary components of the dielectric spectra are linked by Equation 4, then finding a match between fluid and either material's dielectric spectrum should lead to little/no adhesion via vdW forces, enough to significantly reduce or eliminate fouling.

**[0023]** Methods to determine the full dielectric spectra for existing, untabulated  
 20 materials are required. These spectra may be determined directly using a capacitance bridge setup or an ellipsometric measurement, and indirectly by reflectance spectroscopy and VEELS. Additionally the spectra may be obtained by ab initio band structure calculations, such as Density Functional Theory (DFT) simulations. In order to accurately calculate the Hamaker coefficient it is important to have experimental dielectric response data over a wide  
 25 frequency range, from static to IR (important for water) to UV. VEELS enables experimental testing of a very wide range of frequencies (0-100 eV is typical). However, optical reflectance measurements remain the most straightforward to carry out experimentally.

**[0024]** Figure 2 illustrates a diagram of EELS, along with typical VEELS calculated and measured spectra. VEELS is an electron energy-loss technique, which measures the  
 30 amount of energy lost by electrons in single scattering collisions as they traverse through a very thin specimen. The specimen thickness is chosen to be far lower than the electron range in the medium, which ensures almost all single scattering events of the non-transmitted

portion of the electron beam. This provides an additional measure of surety in the measured data, as methods such as DFT directly predict the energy levels of valence electrons, which is what are probed using VEELS. Here, the number of electrons losing a certain amount of energy is measured and tabulated as the arbitrary units of intensity. This, normalized to  
 5 known, absolute values at certain wavelengths (perhaps obtained by reflectance spectroscopy) yields the dielectric spectrum of the material.

**[0025]** In all practical experiments, limitations exist on the upper and lower frequencies that can be tested; however the KK transform requires measurements over an infinite frequency range (as seen in the limits of the integral in Equation 4). Therefore, it is  
 10 conventional to supplement experimental data with approximations for frequencies lower and higher than measured ones. A typical choice for this approximation is a power law  $\varepsilon(\omega) \propto \omega^{-\beta}$  with different values of the exponent  $\beta$  for the high and low sides. This power law approximation is also used to interpolate to frequencies between measured data points. Another choice of approximations is a constant value  $\varepsilon(\omega|\omega < \omega_{\min}) \approx \varepsilon(\omega_{\min})$  for the low  
 15 frequency range corresponding to the minimum measured frequency, and the free electron result  $\varepsilon(\omega|\omega > \omega_{\max}) = 1 - \omega_e^2/\omega^2$  for the high frequency range (where  $\omega_e$  is the plasma frequency of a free electron gas).

**[0026]** Methods for measuring reflectance on materials are well established, as are the transforms to obtain dielectric spectra. Having determined the frequency-dependent  
 20 reflectance, the KK transform is applied to obtain a frequency-dependent phase measurement. The reflectance and phase are combined in a linear system of equations to obtain the frequency-dependent real and imaginary dielectric responses,  $\varepsilon_i(\omega)$ , which is then substituted directly in Equation 4 to yield the dielectric response to imaginary frequency  $\varepsilon_i(\zeta)$ . The force due to van der Waals interactions is then determined by following the Equations 3, 2,  
 25 and 1.

**[0027]** It should be appreciated that the Tabor-Winterton Approximation (TWA), which is valid for materials with similar absorption frequencies  $\omega$  and low refractive indexes  $n$  in the visible spectrum, may be used for an initial candidate material search. The TWA is:

$$30 \quad A_{afb}^{Ham} \approx A_{afb}^{TWA} = \frac{3}{4} kT \left( \frac{\varepsilon_a - \varepsilon_f}{\varepsilon_a + \varepsilon_f} \right) \left( \frac{\varepsilon_b - \varepsilon_f}{\varepsilon_b + \varepsilon_f} \right) + \frac{3\pi h \nu_c}{4\sqrt{2}} \frac{(n_a^2 - n_f^2)(n_b^2 - n_f^2)}{\sqrt{(n_a^2 + n_f^2)(n_b^2 + n_f^2)} (\sqrt{(n_a^2 + n_f^2)} + \sqrt{(n_b^2 + n_f^2)})} \quad (5)$$



In this way, the visible spectrum indices of refraction,  $n$ , along with zero-frequency dielectric constant (polarizability) can be used to take first guesses at which materials should be slick, or fouling-resistant. The goal of finding a material that reduces adhesion is thus methodically approached as finding a material with specific optical properties suited for the system, since  
5 the properties of the fluid and of the fouling particles are already given. The relatively tedious experimental measurements may be significantly expanded by computational analysis of the literature containing measured spectra of materials (applying equations 2 and 3), as well as by modeling of new materials where spectra are calculated based on energy bands from DFT simulations. Due to the vast number of permutations of sample materials to  
10 simulate and a complex dependence of adhesive force on material properties, a genetic algorithm would be appropriate to explore this computational design space.

**[0028]** From the TWA, one way to minimize vdW interaction is to minimize the difference terms in the numerator of Equation 5. Substituting realistic values for the operating conditions, the second term of Equation 5 dominates over the first term. Therefore,  
15 the criterion that the initial candidate fouling resistant materials should have is an index of refraction  $n_a$  close to that of the fluid, and neglecting the first term of Equation 5 for materials whose dielectric properties are not yet known is justified.

**[0029]** In one embodiment, one system of interest includes water-insoluble fluorides, which tend to be quite hard, earth-abundant, and insoluble in water. Figure 3 shows the  
20 Hamaker constants of various materials using full-spectral and Tabor-Winterton calculations. As shown, many of the fluorides possess both low Hamaker constants and indices of refraction.

**[0030]** In one embodiment, with a focus on geothermal power plants, which use high temperature water as the fluid and suffer from SiO<sub>2</sub> particulate fouling, tabulated data can be  
25 used to identify minerals that are water insoluble, relatively hard (to avoid erosion by SiO<sub>2</sub>), and have low refractive indexes, the TWA can be applied to calculate expected vdW forces in water at room temperature. Table 1 summarizes the materials so identified thus far.

Table 1: Candidates for slick surface coatings and indices of refraction compared to those of water and typical passive oxide scales. (Parentheses indicate that dielectric constant data was not available for the approximation.)

Material Type	Name	Formula	Mohs Hardness	Dielec. Const. $\epsilon$	Refract. Index $n$	$A_{\text{ad}}^{\text{max}}$ ( $\mu\text{J}$ )	Ref.
Foulant (b)	Silica	$\text{SiO}_2$	6.5 - 7.0	3.8	1.448	---	[14]
Fluid (f)	Water (25C)	$\text{H}_2\text{O}$	---	80	1.333	---	[14]
Natural oxide surfaces (a)	Magnetite	$\text{Fe}_3\text{O}_4$	5.0 - 6.5	20	2.42	1895	[17]
	Chromia	$\text{Cr}_2\text{O}_3$	8.0 - 8.0	13.3	2.551	1980	[17]
Proposed anti-fouling materials (a)	Calcite	$\text{CaCO}_3$	4	8.67	1.66	448	[17]
	Microcline/Albite	$\text{KAlSi}_3\text{O}_8$	6.0 - 6.5	???	1.52	(268)	N/A
	Olivine	$(\text{Mg, Fe})_2\text{SiO}_4$	6.5 - 7.0	???	1.65	(435)	N/A
	Pyrite	$\text{FeS}_2$	6.0 - 7.0	???	1.75	(360)	N/A
	Fluorite	$\text{CaF}_2$	4	7.4	1.437	195	[14]
	Cryolite	$\text{Na}_3\text{AlF}_6$	2.5 - 3.0	???	1.34	(113)	N/A
	Olivine	$(\text{Mg, Fe})_2\text{SiO}_4$	6.5 - 7.0	???	1.63	(435)	N/A
Muscovite	$\text{KA}(\text{AlSi}_3\text{O}_{10})(\text{F, OH})_2$	5.4-7.0	2.25	1.60	378	[14]	

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**[0031]** With reference to Table 1, note how each of them have visible indices of refraction very close to that of water, compared to the passive oxide layers that normally form on carbon steel ( $\text{Fe}_3\text{O}_4$ ) and stainless steels or nickel-based superalloys ( $\text{Cr}_2\text{O}_3$ ). As can be seen in Table 1, quite a number of materials are sufficiently close to water's index of refraction are predicted to pose a significant improvement over the passive oxides, which naturally grow on structural materials in geofluid or in a nuclear reactor, as examples.

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**[0032]** Figure 4 illustrates one example of a cantilever used to measure the force of adhesion using AFM-FS. Confirmation of the adhesion model comes from directly measuring the force of adhesion using AFM-FS. In this technique, a particle of the foulant/scale material, in this case  $\text{SiO}_2$ , is affixed to the end of a thin SiN cantilever. This cantilever is brought into contact with the surface to be measured, and a laser is bounced off the back of the cantilever, as shown in Figure 4. The deflection of this laser is proportional to the bending of this cantilever, yielding the force required to bend the cantilever (following calibration of its spring constant  $k$ ). Then, the cantilever is pulled up from the surface, and the force required to dislodge the particle is measured using the same technique. It should be appreciated that that contamination from moisture in the air, ions in the water, and ambient hydrocarbons must be taken into account and subtracted in order to acquire accurate AFM-FS data.

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**[0033]** In one embodiment, a vacuum-inert AFM chamber may be used. Figure 5 illustrates a vacuum-inert AFM chamber. As shown, the vacuum chamber allows for pumping the entire system down to  $10^{-3}$  Torr using a turbomolecular pump, while a

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differentially pumped argon ion sputtering gun will be used to sputter-clean the surface of the material to remove oxides and organic contaminants. Without exposure to air, AFM-FS can be performed on the fresh surface in either vacuum or dry inert gas atmosphere.

**[0034]** While the present invention provides a method for reducing or eliminating  
5 fouling on a material or surface through the use of optical properties of a given material and, specifically, using the Hamaker constant as a numerical measure of fouling propensity, an evolutionary algorithm approach such as USPEX, which was optimized to explore the multidimensional space of possible crystal structures and find the most energetically favorable ones, may be used to calculate the Hamaker constant of crystal structures.

**[0035]** Density Functional Theory (DFT) packages, such as VASP (Vienna Ab-initio  
10 Simulation Package), can be used to find frequency-dependent dielectric response as supported by earlier works. Then, a script solves the full-spectrum sum (Equation 2) resulting in a calculated Hamaker constant. The DFT calculation also provides a measure of the energy of the crystal structure, which is an indication of whether the structure is realistic and  
15 stable at the operating conditions.

**[0036]** Figure 6 schematically shows the use of the USPEX algorithm. In the USPEX  
algorithm, crystal structures are optimized in an evolutionary fashion. The algorithm begins by forming random structures that satisfy the initial “hard” constraints such as the number and type of atoms. These structures are then evaluated to obtain a fitness value for each,  
20 which determines whether the structure survives in subsequent generations. In standard usage of USPEX, this fitness value is the overall energy of the structure, which results in the most chemically stable (lowest energy) crystal. For the present invention, the fitness value is instead the Hamaker constant, favoring the structures with lowest adhesion forces. In this case the local energy minimization, which is still required to find realistic materials, is  
25 implemented as a relaxation of the structure in the DFT simulation. The surviving structures are then modified by three operators: heredity, mutation, and permutation. Some of the resulting structures will have more favorable fitness values, and the process is repeated again until a satisfactory number of high-performing structures is found.

**[0037]** Based on the foregoing, it should be appreciated that that many materials may  
30 be selected to provide a “slick” surface to which a foulant or foulant particles will not attach, thus preventing the formation of an initial monolayer that, in turn, precludes continued growth of the foulant or scale. It should further be appreciated that in most cases, the identity or chemical composition of the foulant is not important to the determination of which material of construction or coating to use for a given fluid to which the material or its surface

is exposed. In other words, the selection of the material or material of construction or the coating is universal to each pair of material/coating and working fluid, agnostic of the multitude of potentially fouling materials in a given system. Moreover, because all working fluids in energy systems have visible indices of refraction ranging from 1.2-1.7, the TWA is a valid and accurate estimate of the total vdW force between foulants and material surfaces immersed in a non-vacuum working fluid. Further, because the numerator in the TWA (Equation 5) contains multiples of differences (the  $(n_a^2 - n_f^2)(n_b^2 - n_f^2)$  term), only a near-match between either the working surface (material  $a$ ) and the fluid ( $f$ ) or the fluid and the foulant(s) is required. Because it is easier to control the working surface than to control the foulant(s), only a near match between the working surface and the fluid is required by simply matching the intrinsic index of refraction in the visible or the UV spectrum.

**[0038]** In some embodiments, the material selected matches the visible index of refraction in some portion of the complete optical spectrum of the fluid to which the surface or material is exposed to within  $\pm 20\%$ . In some embodiments, the fluid may be a gas or a liquid and may have a visible index of refraction ranging from 1.00 to 1.76. In some embodiments, the material and may have a visible index of refraction ranging from 1.00 to 1.76 or 1.06 to 1.60. In some embodiments, the material may be solid, bulk material or a coating applied to another material such that the coating modifies the surface chemistry of the underlying material. In some embodiments, the material may be more generally a modification of the surface of the material through a process such as oxidation, fluoridation, surface nitriding, carbon infiltration, etc. In some embodiments, the material may be a crystalline material specifically chosen or designed to match the visible index of refraction of a surrounding fluid in some portion of the complete optical spectrum to within a relative agreement of  $\pm 20\%$ . In some embodiments, the fluid may be water and may not include any foulant. In some embodiments, the fluid may be water and include more than one foulant. In some embodiments, the fluid may be water and the material may have an intrinsic, visible index of refraction ranging from 1.06 to 1.60. In some embodiments, the fluid may be water and the material may contain fluorine. In some embodiments, the fluid may be water and the material may contain a fluorine-bearing crystalline solid. In some embodiments, the fluid may be water and the material may contain fluorite ( $\text{CaF}_2$ ), cryolite ( $\text{Na}_3\text{AlF}_6$ ), albite or microcline ( $\text{KAlSi}_3\text{O}_8$ ). In some embodiments, the material may be an amorphous material specifically chosen or designed to match the visible index of refraction of a surrounding fluid in some portion of the complete optical spectrum to within a relative agreement of  $\pm 20\%$ .

Although the entire optical spectrum (including the visible and non-visible ranges) may be material, in some embodiments, a match is determined within the range of 400-800 nm in the visible spectrum.

**[0039]** It should be appreciated that in some embodiments, the match between the index of refraction of the material and the surrounding fluid may be a match of the ultraviolet (UV) index of refraction as opposed to the visible index of refraction, or the spectral part of the UV range. Although the entire UV spectrum may be material, in some embodiments, a match is determined within the range of 10-400 nm in the UV spectrum.

**[0040]** In some embodiments, the material may be subjected to radiation, such as in a nuclear power plants. In such cases, crud is a form of fouling that degrades the nuclear fuel cladding. Therefore, a material must be selected that provides radiation resistance to retain its properties during use. The fluorine-based minerals described above not only resist radiation damage, but the atomic defects created by irradiation actually enhance their wettability over time and improving their heat transfer properties without sacrificing their fouling resistance. In some embodiments, ZrN and TiC are able to resist crud formation in a PWR environment. In some embodiments, TiN also is able to resist crud formation in a PWR environment.

**[0041]** It should be appreciated that the selection of certain materials for use in constructing surfaces exposed to a fluid that carries a foulant has wide applicability. For example, fouling costs the United States alone \$15 billion in lost revenue in 2013. Every major, energy-intensive heat transfer, energy production, and chemical processing system that contains impurities undergoes fouling, and every one of these systems constitutes a potential revenue stream. For example, the present invention may be used to reduce the buildup of crud on nuclear fuel, the buildup of sludge in secondary heat transfer cycle of nuclear power plants, the buildup of silica on geothermal deep boreholes, the buildup of iron and steel-based corrosion products, as well as "black powder," in the heat exchangers in oil refineries, and the buildup of hard water deposits, which occurs virtually everywhere, including commercial and residential water plumbing systems.

## CLAIMS

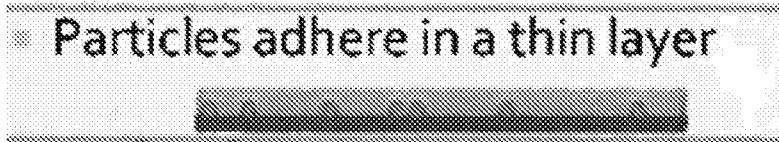
What is claimed is:

1. A method for selecting a material of construction for a surface exposed to a fluid  
5 having a foulant, comprising:  
selecting a material of construction for a surface exposed, during use, to a fluid  
comprising a foulant, wherein the material of construction has an index of refraction that is  
within 20% of an index of refraction of the fluid in some portion of the complete optical  
spectrum.  
10
2. A method for selecting a material of construction for a surface exposed to a fluid  
having a foulant, comprising:  
selecting a coating for a surface exposed, during use, to a fluid comprising a foulant,  
wherein the coating has an index of refraction that is within 20% of an index of refraction of  
15 the fluid in some portion of the complete optical spectrum.
3. A material of construction, comprising:  
a body having a surface that is exposed to a fluid comprising a foulant during use; and  
an index of refraction that is within 20% of an index of refraction of the fluid in some  
20 portion of the complete optical spectrum.
4. A coating for a surface, comprising:  
a coating for a surface that is exposed to a fluid comprising a foulant during use; and  
an index of refraction that is within 20% of an index of refraction of the fluid in some  
25 portion of the complete optical spectrum.
5. The coating of claim 4, wherein said coating is disposed on the surface.

- Operation begins with clean surface



- Particles adhere in a thin layer



- Fouling layer grows



Figure 1

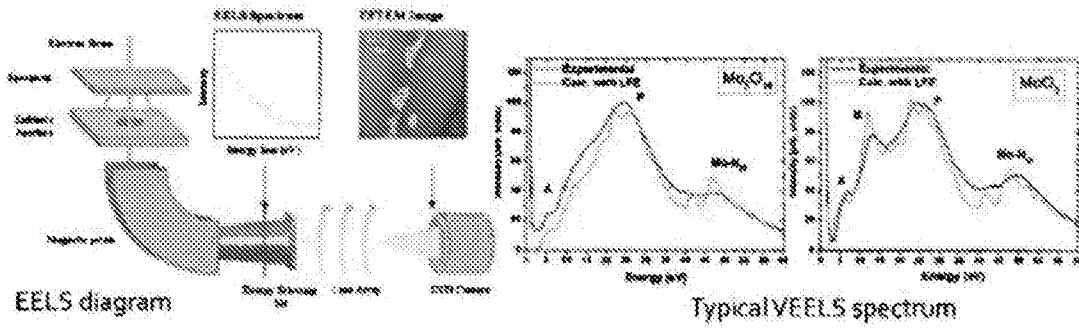


Figure 2

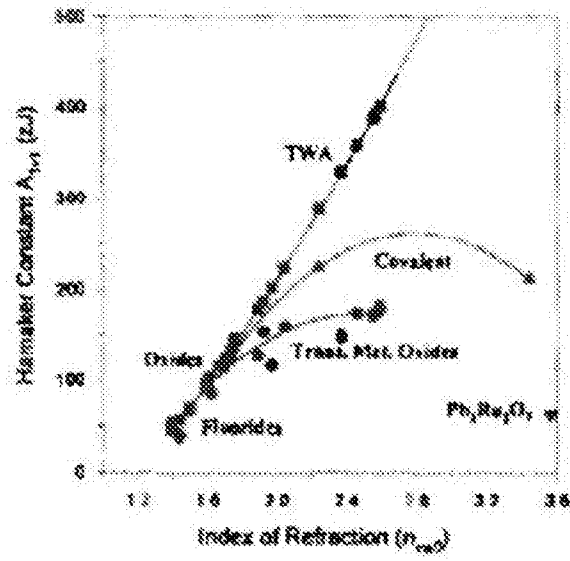


Figure 3

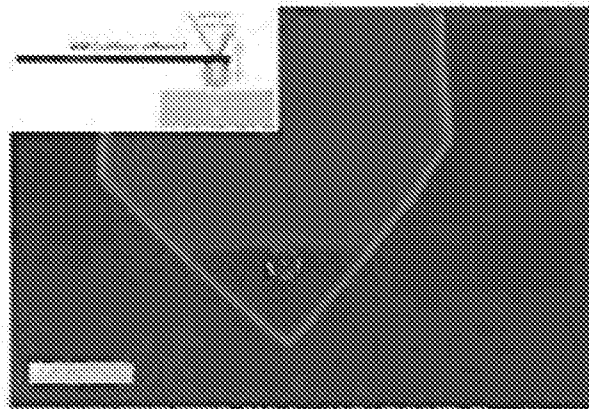


Figure 4



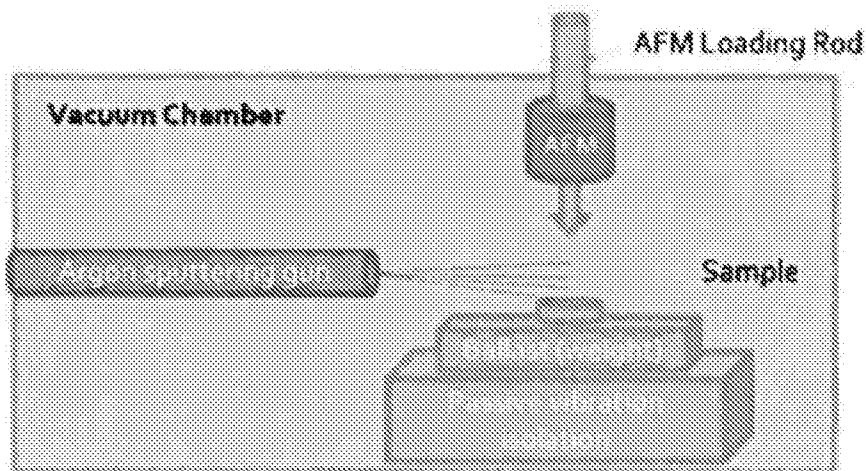


Figure 5

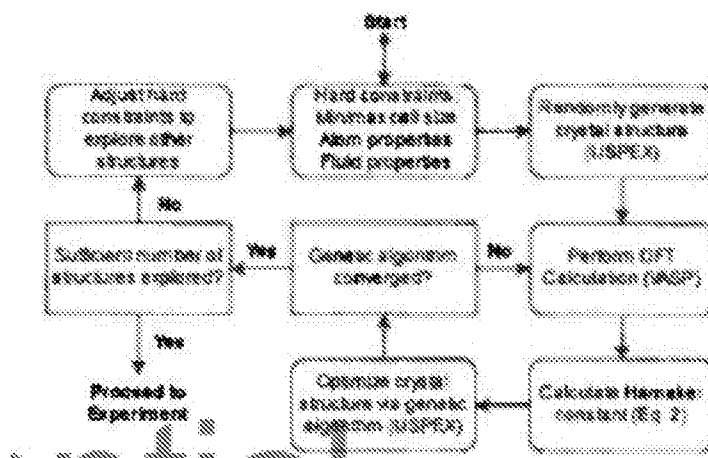


Figure 6

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/53777

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09D 5/16; F28F 19/02; B08B 17/06; C09K 8/52 (2018)

CPC - B63B 59/04; C09D 5/16, C09D 5/1662, C09D 5/1681, C09D 5/1693, C09D 163/00; F28F 19/02; B05D 5/00, B05D 5/08; C02F 2303/20; Y02T 70/32; B08B 17/06, B08B 17/065; C09K 8/52

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)

See Search History Document

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

See Search History Document

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

See Search History Document

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013/0244249 A1 (UNIVERSITY OF WASHINGTON THROUGH ITS CENTER FOR COMMERCIALIZATION) 19 September 2013 (19.09.2013), entire document, especially para [0043], [0004], [0022], [0040], [0249]	1-5
Y	US 2017/0227555 A1 (UNIVERSITY OF WASHINGTON THROUGH ITS CENTER FOR COMMERCIALIZATION) 10 August 2017 (10.08.2017), entire document, especially para [0136], [0075], [0122]	1-5

 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

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"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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

25 November 2018

Date of mailing of the international search report

13 DEC 2018

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