Published online www.heatexchanger-fouling.com

DFT STUDIES ON THE FORMATION OF CaCO₃ DEPOSITIONS ONTO CRISTOBALITE, DIAMOND AND TITANIUM CARBIDE SURFACES

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ABSTRACT

Fouling caused by inversely soluble salts, like CaCO₃, is a general problem on heat transfer surfaces. Carbonate depositions are typically cleanable with acids, but costs of energy losses, operation and maintenance are significant. In this study, formation of CaCO₃ depositions was investigated on cristobalite, diamond and titanium carbide surfaces. The aim of the study was to clarify the detailed mechanisms of crystallization fouling during the initiation on crystalline phases existing in materials used as coatings (SiO_x, TiCN, DLC), and to compare the results to the fouling mechanism of stainless steel (Cr_2O_3).

In experimental studies of fouling, detailed mechanisms and description of sterical and electrostatic factors of surfaces are often very much simplified. In this work, molecular modelling was used to describe surface structures and to investigate the effect of process fluid (water) on the structures. The adsorption of water can be molecular or dissociative. During the dissociative adsorption, hydroxylated surface structures are formed. The existence of hydroxyl groups on the surfaces has an effect on the fouling mechanism. First, the dissociation probability of water on different surfaces was determined according to the adsorption mechanism and energies, and then the attachment of CaCO₃ onto optimized and hydroxylated surfaces was investigated. As a result, the formation mechanism with detailed intermediate steps of CaCO₃ deposition was obtained. The fouling takes place via hydrogen carbonate intermediates, but the final deposition structure was found to vary between surfaces.

INTRODUCTION

Fouling of heat transfer surfaces is a serious problem, and depositions of inversely soluble salts, like calcium carbonate (CaCO₃), are common in industrial processes. Carbonate depositions are typically cleanable with acids, but costs of energy losses, operation and maintenance are significant. Even if numerous cleaning and fouling inhibition chemicals are available on the market, the use of many of these is restricted in EU or will be prohibited by tightening environmental, health and safety legislation. Novel non-fouling materials and new heat exchanger geometries would give sustainable solution to industry in order to mitigate fouling.

Fouling mechanisms can be classified into six groups which are crystallization, particle attachment, chemical fouling, corrosion, biological fouling and solidification (Bott, 1995; Mwaba et al., 2006). The fouling rate, the chemical composition and the physical properties of deposited material on the surfaces depend on process conditions (e.g. pH, temperature, concentrations of soluble species of particles, fluid flow) and construction materials of the heat transfer surfaces (Kostoglou and Karabelas, 1998). In this work, we concentrated on crystallization fouling detected in CaCO₃ solutions. Experimental analysis of depositions gives qualitative and quantitative information on the bulk properties and composition of the depositions. However, it is very demanding to gather information about interaction mechanisms (chemical or physical nature of bonding) between the heat transfer surface and the deposition. Therefore, in addition to laboratory scale fouling experiments, molecular modelling has been applied in this study in order to obtain explanations for the attachment of depositions at the molecular level.

Molecular modelling is a widely applied technique to investigate chemical reactions, properties of solid materials, and attachment of small molecules onto solid surfaces. Investigated systems can be rather complex atomic clusters or periodic model systems (Goniakowski and Gillan, 1996; Ahdjoudj et al., 1999; Lindan et al., 1996; Casarin et al., 1998; Vogtenhuber et al., 1998; Langel, 2002; Diebold, 2003; Menetrey et al., 2003; Bandura et al., 2004; Zhang et al., 2004; Zhang et al., 2007; Teobaldi et al., 2007). In our earlier studies, molecular modelling was already applied as a novel method in the field of fouling research (Puhakka et al., 2007; Puhakka et al., 2008). The molecular modelling was found to be effective in defining reaction path-ways, because process measurements, fouling resistance curves, and composition of depositions can only be used indirectly to determine reaction steps.

In this study, the crystallization fouling caused by $CaCO_3$ solutions was selected because of its importance in several industrial processes, e.g. in dewatering and evaporation processes. In these cases, carbonate salts form depositions typically onto stainless steel surfaces.

Heat exchangers manufactured of stainless steel have a spontaneously formed passive layer, which gives excellent resistance against corrosion. The passive layer consists of chromium oxides and has a thickness of about ten molecular layers (Pießlinger-Schweiger, 2005). However, the oxidation conditions affect significantly the thickness and composition of oxide layers. In addition to chromium oxides, there are manganese and iron oxides with different crystal structures on the outermost layer of stainless steel (Iordanova et al., 1998). In spite of the good corrosion properties, stainless steel is still exposed to sorption of ionic compounds. In order to mitigate the deposition formation and extend the operation period of the heat exchanger, coating materials are developed.

The possibility to use siloxane (SiO_x) , titanium carbonitride (TiCN) and diamond like carbon (DLC) materials as coatings was investigated in this molecular modelling study. Simplified structures of the coatings were used: cristobalite structure of silicon dioxide (SiO₂), diamond and titanium carbide (TiC). Of SiO₂ structures, cristobalite is a high-temperature polymorph of quartz. Diamond was selected to describe in a simplified way the surface structure of amorphous DLC. However, the surface roughness can not be taken into account in this type of modelling. The results obtained for these coatings were compared to those of dichromium trioxide (Cr₂O₃), which was used as a model structure for stainless steel. The investigated coatings were selected based on industrial interest in the aim of eliminating fouling caused by inversely soluble salts, like CaCO₃, on heat transfer surfaces. The objective of the study was to clarify the detailed mechanisms of crystallization fouling during the initiation on crystalline phases existing in materials used as coatings. The results were compared to the fouling mechanism of stainless steel.

METHODS

Methods based on the density functional theory (DFT) were used to investigate the crystal and surface structures of materials intended to be used as coatings of stainless steel heat transfer surfaces. The selected coatings were SiO2 (cristobalite), diamond and TiC. Because water of the process fluids can affect the surface structures and the initiation stage of deposition formation on surfaces, the adsorption mechanism of water onto the surfaces was first investigated. The adsorption of calcium (Ca²⁺) and carbonate (CO_3^{2}) ions onto surfaces and the formation mechanism of CaCO₃ depositions were then determined. All the calculations were performed with the CASTEP (CAmbridge Serial Total Energy Package) code implemented into Materials Studio versions 4.1 (Accelrys, 2006), 4.2 (Accelrys, 2007), 4.3 (Accelrys, 2008a) and 4.3.1 (Accelrys, 2008b). The modelling is based on solving the total electronic energy and overall electronic density distribution in order to define the energetically stable structures for coatings and different adsorbates (Leach, 2001).

During the geometry optimization of the crystal and surface structures of coatings, and adsorption studies of water and Ca^{2+} and CO_3^{2-} ions onto the surfaces, the exchange-correlation was described with the generalized gradient approximation GGA-PBE. As a compromise between the accuracy and computational time, the ultrasoft

pseudopotentials were used for each element. In the potential of titanium, the semicore states were treated as a part of the core. The used potentials were C_00PBE.usp for carbon, Ca_OOPBE.usp for calcium, H_00.usp for hydrogen, O_soft00.usp for oxygen, Si_soft00.usp for silicon, and Ti_00PBE.uspcc for titanium. The kinetic cut-off energy for a plane wave expansion of the wave function was 280 eV. The morphology of the coatings was predicted by using the BFDH (Bravais-Friedel Donnay-Harker) method.

The optimized structures were used in order to calculate energy values for the formation reaction of $CaCO_3$ depositions. The energies were calculated from the singlepoint energies of the ions and the surface structures with and without the adsorbed ions. The calculations were performed using the GGA-RPBE exchange-correlation, and the kinetic cut-off energy was 330 eV.

RESULTS AND DISCUSSION

Crystal Structure of the Coatings

The basic assumption of the research was that the fouling properties of different coatings depend on the atomic layered structure of the coatings. In order to investigate the surface structures, the crystal structures of the coatings have to be known. The starting point for the study has been the XRD determined crystal structures of SiO₂ (a = b = c = 716.0 pm) and diamond (a = b = c = 355.6 pm) with symmetry Fd-3m (Accelrys, 2006), and the crystal structure of TiC (a = b = c = 432.8 pm) with symmetry Fm-3m (Christensen, 1978).

In order to perform molecular modelling studies for the coatings, the lattice parameters of SiO₂, diamond and TiC were calculated. According to the density functional calculations, the lattice parameters of the energetically stable SiO₂, diamond and TiC are a = b = c = 692.4 pm, a = b = c = 357.4 pm and a = b = c = 437.1 pm, respectively (Fig. 1). Comparison to the experimental parameters indicates that the correspondence is good, the differences being only 0.5–3.3%.



Fig. 1 The optimized unit cells of a) TiC, b) diamond and c) SiO_2 (cristobalite).

Surface Structures

Based on the optimized structures, the morphologies of the coatings were predicted by the BFDH method (Fig. 2). The morphologies indicate which surfaces are the typical ones on the heat transfer surfaces. According to the BFDH prediction, there are two dominant surfaces for TiC. These are (111) and (200), the surface areas of which are 78% and 22%. For diamond and SiO₂, there is only one dominant surface, (111). The estimated data of the surface structures were compared to the results of the XRD measurements performed for the deposited TiCN (titanium carbide nitride) and the DLC coatings. The experimental analysis indicated that the TiCN is a crystalline coating. The dominating XRD peaks correspond the (111) and (200) crystal planes of TiC (Fig. 3a). In the case of diamond, the structure of stainless steel substrate dominates the XRD spectrum (Fig. 3b). This means that the DLC coating is mainly amorphous. However, there is a small peak (not detected in the stainless steel spectrum in Fig. 3c) which corresponds to the (111) plane of crystalline diamond. This is an indication that there is also a crystalline phase on the surface structure of DLC coating.. Based on these results, it was supposed that the dominating crystal planes of coatings have a significant role during the deposition formation. Therefore, the (111) surface of the coatings was selected for further studies.



Fig. 2 The estimated morphology of a) TiC, and b) diamond and SiO_2 (cristobalite) by the BFDH method.

After the basic crystal and surface structures of the coatings were determined, the surfaces predicted by BFDH were studied at atomary level. The surface structures were constructed by cleaving them from the optimized crystal structures of coatings. In order to get a more profound description of the sterical and electrostatic factors of the coating surfaces, reconstruction of the surface atom layers was taken into account. In the case of SiO₂ and TiC, it is possible to use the surface structures cleaved from the crystal structures, because the surface structure does not differ significantly from the crystal structures. However, in the case of diamond, the deposition conditions have to be taken into account. When the DLC coating is deposited by plasma enhanced chemical vapour deposition (PECVD) or physical vapour deposition (PVD) techniques, a hydrogen layer exists on the top-most carbon layer (Grill, 1999; Laikhtman et al., 2004). Hydrogen gives the "diamond-like" properties for materials. Therefore, the cleaved (111) surface was covered by hydrogen atoms, and the surface structure was re-optimized in order to obtain a thermodynamically stable surface, describing the real surface structure as precisely as possible (Fig. 4).



Fig. 3 The XRD spectrum of a) TiCN, b) DLC and c) stainless steel.



Fig. 4 The (111) surface of diamond a) without and b) with the hydrogen layer on the surface.

Adsorption of Water onto the Surfaces

From the point of view of potential surface reactions which take place during the deposition formation, it is important that the description of the sterical and electrostatic factors of surfaces is as realistic as possible. It has to be remembered that the coatings are exposed to the effects of the species of the process liquors. Of these species, water is the most significant adsorbate which has an effect on the properties of solid surfaces and surface. Therefore, the adsorption of water onto the coatings was investigated.

Water can adsorb onto solid surfaces as a molecule, or it can dissociate forming partially or fully hydroxylated surfaces (Cappus et al., 1993; Maurice et al., 2001; Henderson et al., 2000; Henderson, 2002; Kim et al., 2003; Asay and Kim, 2005; Ignatchenko et al., 2006; Yang and Wang, 2006; Saunders et al., 2008). Therefore, the investigated surfaces were covered by water molecules or hydroxyl groups and protons (dissociated water molecule), and the modified surface was allowed to relax a stable surface structure. The reaction energy for the dissociation of water molecules on the surfaces was then calculated.

On the (111) surface of TiC, water adsorbs onto the surface and then dissociates forming a surface hydroxyl group bonded with a titanium atom and a proton bonded with a carbon atom

$$S-H_2O \rightarrow S-OH + S-H \tag{1}$$

The energy released in this reaction is -2.47 eV (Fig. 5). On the (111) surface of SiO₂, only one half of water molecules dissociate forming a partially hydroxylated surface

$$2 \text{ S-H}_2\text{O} \rightarrow \text{S-H}_2\text{O} + \text{S-OH} + \text{S-H}$$
(2)

The energy for this reaction is -4.78 eV, and the energy barrier for water dissociation is 0.74 eV (Fig. 6). This corresponds the values 0.3-1.1 eV reported in literature (Yang and Wang, 2006). On the (111) surface of diamond, water does not dissociate, if the adsorbed hydrogen layer exists on the surface. The adsorption energy of water is only -0.05 eV. Based on these results, it could be concluded that the adsorbed water molecules dissociate rather easily, forming the layered structure of hydroxyl groups onto the TiC and SiO₂ surfaces. Therefore, the deposition formation studies were performed using the hydroxylated TiC surfaces and partially hydroxylated SiO₂ surfaces. In the case of diamond, the surface structure consists of the adsorbed hydrogen layer and adsorbed water molecules. These surfaces were supposed to describe the real heat transfer surfaces as realistic as possible.

Deposition Formation on the Surfaces

In the deposition formation reaction, the interest was on chemical reactions during the initiation stage of fouling. The focus was on inversely soluble calcium carbonate (CaCO₃) salt, and its depositions on coating surfaces. The aim was to clarify the detailed mechanisms of crystallization fouling during the initiation. The study was started by determining the adsorption positions and energies of a calcium (Ca²⁺) ion on the coating surfaces. After that a carbonate (CO_3^{2-}) ion was adsorbed onto the Ca²⁺ covered surfaces. By optimizing the positions of Ca²⁺ and CO₃²⁻ on the surfaces at the same time, the bonding geometry of CaCO₃ on different surfaces was achieved. The initial structure of the ionic compound and its stability was checked by adding a water molecule onto the surface and calculating again the structure of the CaCO₃ at the presence of water. As a result, the detailed reaction mechanisms were obtained for the formation of CaCO₃ deposition on the (111) surfaces of TiC (Fig. 7), SiO₂ (Fig. 8) and diamond (Fig. 9).



Fig. 5 Dissociated water molecules on the (111) surface of TiC. Big dark grey spheres: carbon. Small light grey spheres: titanium.



Fig. 6 Dissociated water molecules on the (111) surface of SiO₂. Yellow spheres: silicon. Red spheres: oxygen. White spheres: hydrogen.

According to the calculated results, the adsorption of Ca^{2+} onto the coating surfaces depends on the coating materials. On the TiC surface, the adsorption energy is -5.18 eV, and on the diamond surface, it is -5.00 eV. On the other hand, on the SiO₂ surface, the interaction of Ca^{2+} with the surface is repulsive, and adsorption is not favourable.

Comparison of the species and the intermediate steps of the reaction during the deposition formation indicated that fouling takes place via a hydrogen carbonate (HCO₃⁻) intermediate on the TiC and SiO₂ surfaces. Only on the diamond surface, the reaction proceeds directly to the end product, CaCO₃. On all the surfaces, the role of the hydrogen bonding of water is very significant during the deposition formation. The total energies for the investigated reactions during the CaCO₃ deposition on the (111) surfaces of TiC, SiO_2 and diamond are -4.74 eV, -9.33 eV and -3.31 eV, respectively.



S-O---HCO3Ca--- H2O + S-H

Fig. 7 Formation of CaCO₃ deposition on the (111) surface of TiC. Big dark grey spheres: carbon. Small light grey spheres: titanium. Green spheres: calcium. Red spheres: oxygen. White spheres: hydrogen.

The surface structures of stainless steel were already investigated by Puhakka et al. (2008). The uppermost layer structure of stainless steel was described using Cr₂O₃ as a model for the surface. It was supposed that the (004) surface of Cr₂O₃ corresponds the corrosion protective chromiumrich layer. When the adsorption of water was investigated, it was concluded that the dissociative adsorption is possible, but it is more presumable that water adsorbs in a molecular form. The calculated adsorption energy was very weak, only -0.06 eV. Now the formation of CaCO₃ deposition was investigated on the (004) surface of Cr₂O₃ with an adsorbed water layer. The results are presented in Fig. 10. The total energy for this reaction is -3.15 eV, and it is smaller than on the other investigated coating surfaces. The corresponding energy for the non-hydroxylated (10-2) surface of Cr₂O₃ is -3.00 eV (Puhakka et al., 2008). According to the calculated results, the investigated coatings can not mitigate the formation of CaCO₃ depositions.



Fig. 8 Formation of CaCO₃ deposition on the (111) surface of SiO₂. Yellow spheres: silicon. Red spheres: oxygen. Green spheres: calcium. Grey spheres: carbon. White spheres: hydrogen.



Fig. 9 Formation of CaCO₃ deposition on the (111) surface of diamond. Grey spheres: carbon. White spheres: hydrogen. Green spheres: calcium. Red spheres: oxygen.



Fig. 10 Formation of $CaCO_3$ deposition on the fully oxidized (004) surface of Cr_2O_3 where the top layer consists of only oxygen atoms. Red spheres: oxygen. Green spheres: calcium. Grey spheres: carbon. White spheres: hydrogen.

The crystallization fouling of CaCO₃ onto stainless steel surface was also investigated in a laboratory scale apparatus (Pääkkönen et al., 2009). The aim was to clarify the crystallinity of the deposits on the surfaces. It was found that the crystallization takes place in the bulk solution in addition to the surface but the effect of bulk precipitation is minimized by using filters in-line of the experimental apparatus. Based on XRD analysis, varying amounts of both aragonite and calcite was found from the deposition on the surface. The SEM (Scanning Electron Microscopy) analyses (Fig. 11) showed that the deposited material contains orthorhombic, needle shaped crystals and hexagonal, round shaped particles. These different morphological structures are going to compare to the modelled results, but so far our models have been too simplified for the structural analysis of CaCO₃ depositions.



Fig. 11 Different morphologies of CaCO₃ found from the deposition on the stainless steel surface.

CONCLUSIONS

Molecular modelling was used in studying the formation of $CaCO_3$ depositions on different coating surfaces. In particular, the initiation mechanism of crystallization fouling was determined on the SiO₂, diamond

and TiC surfaces at the molecular level. As a result, the formation mechanism with detailed intermediate steps for $CaCO_3$ deposition was obtained. The fouling takes place mainly via HCO_3^- intermediates, and the final deposition structure was found to vary between surfaces. Based on these calculated results, it was possible to rank these coatings against $CaCO_3$ deposition formation. The results will be verified by fouling experiments for coatings and stainless steel in a laboratory scale apparatus.

ACKNOWLEDGEMENTS

This work was a part of the FOULSURFACE project which was carried out in MATERA ERA-Net cooperation with VTT Technical Research Centre of Finland (VTT), University of Oulu, SINTEF and University College Dublin. The project is jointly funded by Tekes, The Research Council of Norway, Enterprise Ireland, VTT, SINTEF and seven industrial companies from Finland, Sweden and Austria. Financial support also from the Graduate School for Energy Science and Technology (EST), Jenny and Antti Wihuri Foundation, and Tauno Tönning Foundation is obtained. The authors thank the research partners and funding organizations.

NOMENCLATURE

BFDH	Bravais-Friedel Donnay-Harker method
CASTEP	CAmbridge Serial Total Energy Package
DLC	Diamond Like Carbon
GGA-PBE	Perdew, Burke and Ernzerhof version of
	generalized gradient approximation functional
GGA-RPBE	Hammer, Hansen, Norskov modified Perdew,
	Burke and Ernzerhof version of generalized
	gradient approximation
PVD	Physical Vapour Deposition
PECVD	Plasma Enhanced chemical vapour deposition
SEM	Scanning Electron Microscopy
Surf	Surface
XRD	X-Ray Diffraction

REFERENCES

Accelrys, 2006, *MS Modeling*, Release 4.1. San Diego: Accelrys Software Inc.

Accelrys, 2007, *MS Modeling*, Release 4.2. San Diego: Accelrys Software Inc.

Accelrys, 2008a, *MS Modeling*, Release 4.3. San Diego: Accelrys Software Inc.

Accelrys, 2008b, *MS Modeling*, Release 4.3.1. San Diego: Accelrys Software Inc.

Asay, D. B., and Kim, S. H., 2005, Evolution of the Adsorbed Water Layer Structure on Silicon Oxide at Room Temperature, *J. Phys. Chem. B*, Vol. 109, pp. 16760–16763.

Ahdjoudj, J., Markovits, A., and Minot, C., 1999, Hartree-Fock periodic study of the chemisorption of small molecules on TiO₂ and MgO surfaces, *Catalysis Today*, Vol. 50, pp. 541–551.

Bandura, A. V., Sykes, D. G., Shapovalov, V., Troung, T. N., Kubicki, J. D., and Evarestov, R. A., 2004, Adsorption of Water on the TiO₂ (Rutile) (110) Surface: A

Comparison of Periodic and Embedded Cluster Calculations, J. Phys. Chem. B, Vol. 108, pp. 7844–7853.

Bott, T. R., 1995, *Fouling of Heat Exchangers*, Elsevier, Amsterdam.

Bredow, T., 1998, Embedded cluster study of water adsorption at Cr_2O_3 (0001), *Surf. Sci.*, Vol. 401, pp. 82–95.

Cappus, D., Ehrlich, C. X. D., Dillmann, B., Ventrice, C. A. Jr., Shamery, K. A., Kuhlenbeck, H., and Freund, H.-J., 1993, Hydroxyl groups on oxide surfaces: NiO(100), NiO(111) and $Cr_2O_3(111)$, *Chem. Phys.*, Vol. 177, pp. 533–546.

Casarin, M., Maccato, V., and Vittadini, A., 1998, Molecular Chemisorption on $TiO_2(110)$: A Local Point of View, *J. Phys. Chem. B*, Vol. 102, pp. 10745–10752.

Christensen, A. N., 1978, The temperature factor parameters of some transition metal carbides and nitrides by single crystal X-ray and neutron diffraction, *Acta Chem. Scand.*, *Series A*, Vol. 32, pp. 89–90.

Diebold, U., 2003, The surface science of titanium dioxide, *Surf. Sci. Rep.*, Vol. 48, pp. 53–229.

Grill, A., 1999, Diamond-like carbon: state of the art, *Diam. Relat. Mater.*, Vol. 8, pp. 428–434.

Goniakowski, J., and Gillan, M., 1996, The adsorption of H_2O on TiO_2 and SnO_2 (110) studied by first-principles calculations, *Surf. Sci.*, Vol. 350, pp. 145–158.

Henderson, M. A., and Chambers, S. A., 2000, HREELS, TPD and XPS study of the interaction of water with the α -Cr₂O₃(001) surface, *Surf. Sci.*, Vol. 449, pp. 135–150.

Henderson, M. A., 2002, The interaction of water with solid surfaces: fundamental aspects revisited, *Surf. Sci. Rep.*, Vol. 46, pp. 1–308.

Ignatchenko, A., Nealon, D. G., Dushane, R., and Humphries, K., 2006, Interaction of water with titania and zirconia surfaces, *J. Mol. Cat. A: Chem.*, Vol. 256, pp. 57–74.

Iordanova, I., Forcey, K. S., Harizanova, R., Georgiev, Y., and Surtchev, M., 1998, Investigation of structure and composition of surface oxides in a high chromium martensitic steel, *J. Nucl. Mater.*, Vol. 257, pp. 126–133.

Kim, Y. D., Wei, T., Stultz, J., and Goodman, D. W., Dissociation of Water on a Flat, Ordered Silica Surface, *Langmuir*, 2003, Vol. 19, pp. 1140–1142.

Kostoglou, M., and Karabelas, A. J., 1998, Comprehensive Modeling of Precipitation and Fouling in Turbulent Pipe Flow, *Ind. Eng. Chem. Res.*, Vol. 37, pp. 1536–1550.

Laikhtman, A., Lafosse, A., Coat, Y. L., Azria, R., and Hoffman A., 2004, Interaction of water vapor with bare and hydrogenated diamond film surfaces, *Surf. Sci.*, Vol. 551, pp. 99–105.

Langel, W., 2002, Car-Parrinello simulation of H_2O dissociation on rutile, *Surf. Sci.*, Vol. 496, pp. 141–150.

Leach, A. R., 2001, *Molecular Modelling, Principles* and *Applications*, 2nd ed., Pearson Education Limited, Essex.

Lindan, P. J. D., Harrison, N. M., Holender, J. M., and Gillan, M. J., 1996, First-principles molecular dynamics

simulation of water dissociation on TiO_2 (110), *Chem. Phys. Lett.*, Vol. 261, pp. 246–252.

Maurice, V., Cadot, S., and Marcus, P., 2001, Hydroxylation of ultra-thin films of α -Cr₂O₃ (0 0 0 1) formed on Cr (1 1 0), *Surf. Sci.*, Vol. 471, pp. 43–58.

Menetrey, M., Markovits, A., and Minot, C., 2003, Reactivity of a reduced metal oxide surface: hydrogen, water and carbon monoxide adsorption on oxygen defective rutile TiO₂(110), *Surf. Sci.*, Vol. 524, pp. 49–62.

Mwaba, M. G., Golriz, M. R., and Gu, J., 2006, A semiempirical correlation for crystallization fouling on heat exchange surfaces, *App. Therm. Eng.*, Vol. 26, pp. 440–447.

Pießlinger-Schweiger, S., 2005, Surface treatment of metallic heat exchangers, *Heat Exchanger Fouling and Cleaning - Challenges and Opportunities*, Kloster Irsee, Germany, June 5–10, 2005, Engineering Conferences International, Brooklyn, NY, USA.

Puhakka, E., Riihimäki, M., and Keiski, R. L., 2007, Molecular Modeling Approach on Fouling of the Plate Heat Exchanger: Titanium Hydroxyls, Silanols, and Sulphates on TiO₂ Surfaces, *Heat Transfer Eng.*, Vol. 28, pp. 248–254.

Puhakka, E., Riihimäki, M., and Keiski, R. L., 2008, Fouling mechanisms by *ab initio* calculations – Condensation reactions on the rutile (101) surface and adsorption of ions on the Cr_2O_3 surfaces, *Proceedings of the 7th International Conference on Heat Exchanger Fouling and Cleaning* – *Challenges and Opportunities*, eds. H. Müller-Steinhagen, M. R. Malayeri, and A. P. Watkinson, ECI Symposium series, Tomar, Portugal, July 1–6, 2007, The Berkeley Electronic Press, Vol. RP5, pp. 300–307.

Pääkkönen, T. M., Riihimäki, M., Puhakka, E., Muurinen, E., Simonson, C. J., and Keiski, R. L., 2009, Crystallization fouling of $CaCO_3$ in plate heat exchanger – Effect of bulk crystallization on mass deposition on the surface, *International Conference on Heat Exchanger Fouling and Cleaning* – 2009, manuscript.

Saunders, S. R. J., Monteiro, M., and Rizzo, F., 2008, The oxidation behaviour of metals and alloys at high temperatures in atmospheres containing water vapour: A review, *Prog. Mater. Sci.*, Vol. 53, pp. 775–837.

Teopaldi, G., Hofer, W. A., Bikondoa, O., Pang, C. L., Cabailh, G., and Thornton, G., 2007, Modelling STM images of $TiO_2(110)$ from first-principles: Defects, water adsorption and dissociation products, *Chem. Phys. Lett.*, Vol. 437, pp. 73–78.

Vogtenhuber, D., Podloucky, R., and Redlinger, J., 1998, Ab initio studies of H_2O adsorption on the $TiO_2(110)$ rutile surface, *Surf. Sci.*, Vol. 402-404, pp. 798–801.

Yang, J., and Wang, E. G., reaction of water on silica surfaces, *Curr. Opin. Solid State Mater.* Sci., Vol. 10, pp. 33–39.

Zhang, Z., Fenter, P., Cheng, L., Sturchio, N. C., Bedzyk, M. J., Předota, M., Bandura, A., Kubicki, J. D., Lvov, S. N., Cummings, P. T., Chialvo, A.A., Ridley, M.K., Bénéseth, P., Anovitz, L., Palmer, D. A., Machesky, M. L., and Wesolowski, D. J., 2004, Ion Adsorption at the Rutile-Water Interface: Linking Molecular and Macroscopic Properties, *Langmuir*, Vol. 20, pp. 4954–4969. Zhang, Z., Fenter, P., Sturchio, N. C., Bedzyk, M. J., Machesky, M. L., and Wesolowski, D. J., 2007, Structure of rutile TiO_2 (110) in water and 1 molal Rb⁺ at pH 12: Interrelationship among surface charge, interfacial hydration

structure, and substrate structural displacements, *Surf. Sci.*, Vol. 601, pp. 1129–1143.