

FOULING MECHANISMS BY *AB INITIO* CALCULATIONS - CONDENSATION REACTIONS ON THE RUTILE (101) SURFACE AND ADSORPTION OF IONS ON THE Cr₂O₃ SURFACES

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ABSTRACT

Molecular modelling approach was utilized to describe detailed fouling mechanism caused by crystallization. The interest was on the heat transfer surfaces, which were manufactured from titanium and stainless steel. With *ab initio* calculations, the role of the surface oxide layer structure of titanium and stainless steel on fouling was investigated. The surface structure of titanium and stainless steel were assumed to consist of rutile (TiO₂) and dichromium trioxide (Cr₂O₃), respectively. It was found that the inorganic fouling depends strongly on the oxide layer structure and the existence of hydroxyl groups on the surface. Based on the results, two mechanistically different fouling categories were found. When the surface hydroxyl groups exist, the fouling can take place via condensation reactions with species containing hydroxyl groups. On surfaces without the surface hydroxyl groups, fouling takes place preferably via adsorption of ions.

INTRODUCTION

Fouling in industrial heat transfer units and related equipment is a serious problem causing enormous cleaning and maintenance costs. 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 heat transfer surfaces (Kostoglou and Karabelas, 1998). Experimental analysis of depositions gives qualitative and quantitative information on the bulk properties and composition of depositions. However, it is very demanding to gather information about interaction mechanisms (chemical or physical nature of bonding) between heat transfer surfaces and depositions. Therefore, molecular modelling has been applied in this study in order

to obtain explanations for the attachment of depositions at the molecular level.

Molecular modelling techniques have been widely used to estimate chemical reactions between single atoms or small molecules, properties of solid materials, and adsorption behaviour of small molecules on solid surfaces. Nowadays, with increased computer power rather complex atomic cluster or periodic model systems can be calculated (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), which enables even practical engineering problems to be solved. In our earlier study, molecular modelling was already applied as a novel method in the field of fouling research (Puhakka et al., 2007). The main advance of the molecular modelling was found in defining reaction path-ways which may not be defined from process measurements and fouling resistance curves.

In this study, the compounds for the modelling have been selected to have industrial interest. The modelled cases of crystallization fouling exist e.g. in titanium dioxide pigment precipitation, power plant sea water cooling, calcite pigment dewatering and black liquor evaporation train. In these cases, transition metal hydroxyls and silanol species form depositions onto the surfaces of titanium heat exchangers (Puhakka et al., 2007), and alkali and alkali earth metal cations onto stainless steel surfaces.

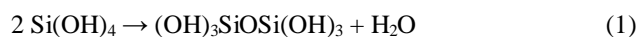
Heat exchangers manufactured from titanium metal (Sul et al., 2001) and stainless steel have spontaneously formed a surface oxide layer. The oxide layer gives excellent resistance against corrosion for titanium materials (Leng et al., 2004) and stainless steel, and the layers consist of titanium dioxide and chromium-rich oxide, respectively. According to Diebold's (2003) recent wide review on surfaces of TiO₂, surface may coexist in four different crystal structures: anatase, brookite, cotunnite and rutile. Of these, anatase, brookite and rutile can be formed in normal pressure (Jalava et al., 1998). In order to produce cotunnite,

high pressure and temperature will be needed. This crystal structure belongs to one of the hardest known oxide materials (Dubrovinsky et al., 2001). However, rutile and anatase are the most important ones in the applications of TiO_2 (Diebold, 2003). Because the rutile structure is thermodynamically more stable than the anatase structure, it is quite evident that the stable oxide layer of passivated surface of metallic titanium can be considered as rutile. The complete titanium-oxygen system and its phases are thermodynamically assessed by Waldner and Eriksson (1999).

Also, the properties of stainless steel are based on the passive layer on the surface. It mainly 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).

Transition metals and silicates exist in many hydrated forms in aqueous solutions. E.g. in aqueous solutions of sulfuric acid, titanium(IV) can exist in forms, which can be presented with the formula $\text{Ti}(\text{OH})_x^{(4-x)+}$; $x < 4$ (Comba and Merbach, 1987; Sugimoto et al., 2002). Strong complexation of titanium with SO_4^{2-} is known (Beukenkamp and Herrington, 1960) as well other complexes of form $[\text{Ti}(\text{OH})_n\text{L}_m]^{(4-n-m)+}$ are reported. Olation and oxolation reactions, where multinuclear polymeric species are formed are typical in concentrated titanium solutions. These reactions are referred also condensation polymerization, because the reaction produces water molecules when oxo-bridge $-\text{O}-$ or olo-bridge $-\text{OH}-$ is formed between titanium atoms. According to our thermodynamic analysis (Puhakka et al., 2007), the soluble species, $\text{Ti}(\text{OH})_4$, was chosen to a model compound in order to describe interactions between the process fluid and heat transfer surface.

The dissolution of silicates involves a chemical reaction or hydrolysis in an excess of water. In acidic conditions, neutral complexes are dominant (Baes and Mesmer, 1976). Low condensation polymers, multinuclear complexes, similar to titanium are typical. The polymerization is thought to occur by condensation of silanol ($-\text{SiOH}$) groups, thus the initial step in polymerization is



In the polymerization, chain, ring and more complex 3D network structures of numerous siloxane units $-\text{Si}-\text{O}-\text{Si}-$ is formed. This will result in an amorphous silica precipitate (Terry, 1983). For silicon a neutral compound, $\text{Si}(\text{OH})_4$, comparable to titanium species, was selected as the fouling compound in the modelling.

The surface complex formation of an ion on the oxide surface may form inner-sphere complex ("chemical bond"), an outer-sphere complex ("ion pair") or be in the diffuse layer of surrounding process fluid (Stumm, 1992). In the case of stainless steel, we focused on depositions formed by salts of alkali and alkali earth metal cations. The counter-ion was carbonate or sulphate ion. Accordingly to Baes and Mesmer (1976) these species do not form multinuclear complexes, single anions and cations were used in modelling.

The aim of the molecular modelling work was to clarify, if there is any chemical explanation at molecular level for the inorganic fouling of heat exchangers manufactured from titanium and stainless steel. Further, the clarification of the oxide layer structure of titanium and stainless steel and observation of structural differences between materials were the important focus areas of the research.

METHODS

Density functional methods were used to investigate the crystal and surface structures of rutile and Cr_2O_3 , and the adsorption of titanium and silicon hydroxyls compounds onto the rutile surfaces, and the adsorption of different ions onto the Cr_2O_3 surfaces. In the density functional calculations, the total electronic energy and overall electronic density distribution are solved in order to define the energetically stable structures for chemical compounds and reaction intermediates (Leach, 2001).

Ab initio quantum mechanics calculations were performed with the CASTEP code implemented into Cerius² version 4.6 (Accelrys, 2001) and Materials Studio versions 3.0 (Accelrys, 2003), 3.1 (Accelrys, 2004), 3.1.5 (Accelrys, 2005) and 3.2 (Accelrys, 2005). During the geometry optimization of the crystal and surface structures, the exchange-correlation was described with generalized gradient approximation GGA-PW91 for rutile structures and GGA-PBE for Cr_2O_3 structures. As a compromise between the accuracy and computational time of calculations, the ultrasoft pseudopotentials were used for each element. In the potential of titanium and chromium, the semicore states were treated as a part of the core. The kinetic cut-off energy for a plane wave expansion of the wave function was 280 eV for rutile structures, 260 eV for Cr_2O_3 structures and 330 eV for Cr_2O_3 structures in the presence of sodium. The morphology of rutile and Cr_2O_3 was predicted by using the BFDH method.

In the reaction path calculations of titanium and silicon hydroxyl compounds on the rutile surfaces, the exchange-correlation potential was GGA-PBE, and the kinetic cut-off energy was 280 eV. The adsorption energies of ions on the Cr_2O_3 surfaces were calculated from the single-point 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

The basic assumption of the research was that the excellent corrosion resistance of titanium and stainless steel is based on their surface oxide layers, titanium dioxide layer and chromium-rich oxide layer, respectively. In the case of titanium, it was supposed that the oxide layer consists of thermodynamically stable tetragonal rutile structure ($a = b = 459.4$ pm, $c = 295.9$ pm and $c/a = 0.644$) with symmetry $P42/mnm$ (Accelrys, 2001). For stainless steel, the choice of surface model structure was not so obvious, because the chemical composition of the oxide layer is dependent on the type of stainless steel. In this research, a simple surface model structure was preferred, so that the hexagonal Cr_2O_3 ($a = b = 495.9$ pm, $c = 1359.3$ pm and $c/a = 2.741$) with symmetry $R-3c$ (Accelrys 2004) was chosen for the surface model.

In order to perform molecular modelling studies for the metal oxide surfaces, the calculated lattice parameters of rutile and Cr_2O_3 were determined. According to the density functional calculations, the lattice parameters of the energetically stable rutile structure are $a = b = 470.2$ pm, $c = 301.7$ pm and $c/a = 0.642$ (Fig. 1a). A comparison of the results to the experimental parameters indicates that the correspondence between the calculated and experimental parameters are good. Based on the optimized structure, the morphology of rutile was predicted by the BFDH method (Puhakka et al., 2007). The morphology indicates which surfaces are typical ones on the heat transfer surfaces. According to the BFDH prediction, there are two dominant plane surfaces: (110) and (101). The estimated surface areas are 59.4 % and 40.6 %, respectively.

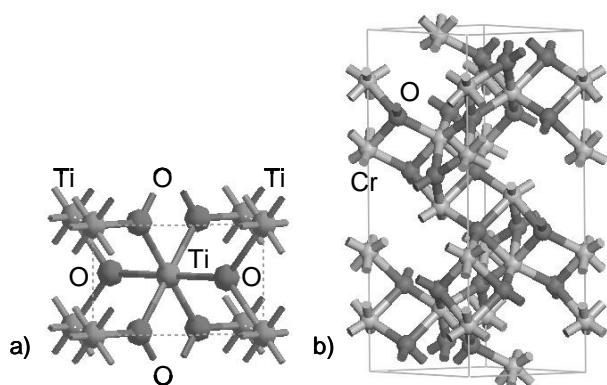


Fig. 1 The optimized unit cells of a) rutile and b) Cr_2O_3 .

The calculated lattice parameters of energetically stable Cr_2O_3 are $a = b = 513.8$ pm, $c = 1403.6$ pm and $c/a = 2.732$ (Fig. 1b). In this case, the correspondence between the calculated and experimental parameters is also good. The

morphology of the Cr_2O_3 crystal was also predicted by the BFDH method. There are three dominant surfaces: (10-2), (104) and (006). The estimated surface areas are 90.6 %, 8.6 % and 0.8 %, respectively (Fig. 2).

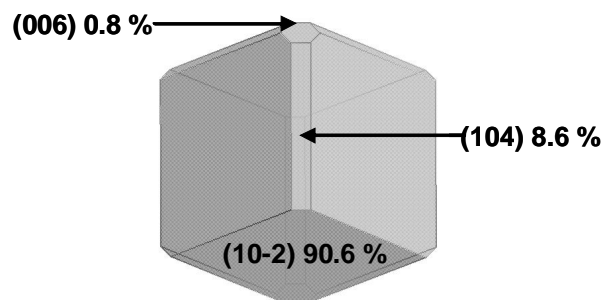


Fig. 2 The estimated morphology of Cr_2O_3 by the BFDH method.

After the basic structure of rutile (TiO_2) and Cr_2O_3 have been determined, then the atomic structure of the BFDH predicted surfaces has to be considered. Of the rutile surfaces, the most relevant surfaces are so-called autocompensated surfaces where the same number of Ti-O and O-Ti bonds are broken on the outermost atomic layer (Diebold, 2003). The autocompensated (110) and (101) surfaces of rutile have been presented in our earlier research (Puhakka et al., 2007). On the (110) surface, the titanium atoms are five- or six-coordinated, and there are bridge oxygen atoms on the surface. On the (101) surface, the titanium atoms are five-coordinated. The typical coordination number of the titanium atom in the bulk rutile is six. Therefore, the surfaces where the coordination number of the titanium is under six are interesting ones, because the vacancy site increases the sensitivity of the rutile for potential surface reactions.

On the (10-2) and (104) surfaces of Cr_2O_3 , the chromium atoms are five-coordinated, and on the (006) surface, the chromium atoms are three-coordinated (Fig. 3a and 3b). Because the coordination number of chromium is always under six on these surfaces estimated by the BFDH method, a surface with six-coordinated chromium atoms were also taken into account in this research. The surface with six-coordinated atoms is selected, because in the bulk structure of Cr_2O_3 , the chromium is six-coordinated like titanium in the bulk rutile. Based on this, it can be assumed that the chromium atom is also fully coordinated in the corrosion protective chromium-rich layer. Therefore, the (004) surface was also included into the research in order to describe a fully oxidated chromium oxide surface (Fig. 3c).

From the point of view of potential surface reactions, it is important that the description of the sterical and electrostatic factors of surfaces is as realistic as possible. Therefore, the reconstruction of the surface atom layers was

taken into account. As an example, the optimized surface structures of Cr_2O_3 are presented in Fig. 3. In the process conditions, these clean heat transfer surfaces are affected by species in process liquor. In most processes, water is the most significant adsorbate which has an effect on the properties of solid surfaces. Therefore, the adsorption of water onto the rutile and Cr_2O_3 surfaces was investigated.

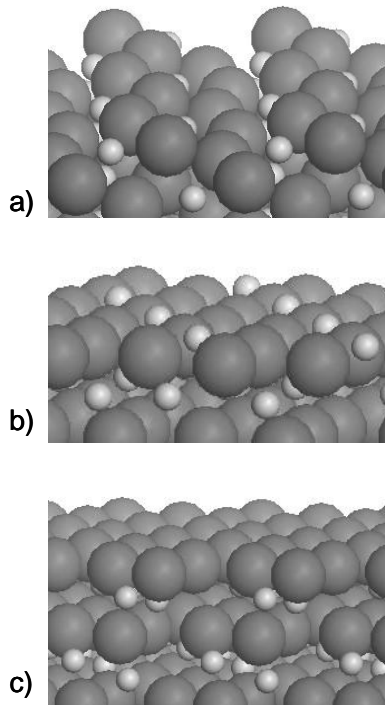


Fig. 3 The optimized surface structures of Cr_2O_3 : a) the (10-2) surface with five-coordinated Cr atoms, b) the (006) surface with three-coordinated Cr atoms, and the (004) surface with six-coordinated Cr atoms. Small grey circles: Cr atoms. Big grey circles: O atoms.

Water can adsorb onto solid surfaces as a molecule, or it can dissociate forming partially or fully hydroxylated surfaces. The behaviour of the water molecule on different rutile surfaces has been investigated in many studies (Goniakowski and Gillan, 1996; 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). Recently, experimental and theoretical studies have been indicated that the water layer exists on the oxygen terminated rutile (110) surface (Zhang et al., 2004; Zhang et al., 2007). However, the proportion of the molecularly and dissociatively adsorbed water depends on the pH. At near-neutral pH, the molecular adsorption dominates, but at pH 12, the proportion of the dissociative adsorption increases.

Further, it has been indicated that the molecular adsorption is favourable in the case of the monolayer coverage, but the dissociative adsorption comes more favourable in the half-monolayer (Bandura et al., 2004).

At that time, our research concerning the fouling on the rutile surfaces started, most theoretical studies predicted that water adsorbs onto the (100) and (110) rutile surfaces dissociatively (Goniakowski and Gillan, 1996; Lindan et al., 1996; Langel, 2002; Diebold, 2003; Menetrey et al., 2003). Based on these results, it was assumed that adsorption of water is also dissociative on the autocompensated (101) surface where all titanium atoms are five-coordinated (Puhakka et al., 2007). Therefore, the TiO_2 surface was covered by hydroxyl groups, and the modified surface structure was allowed to relax in order to receive the stable hydroxylated surface for our fouling reaction mechanism studies.

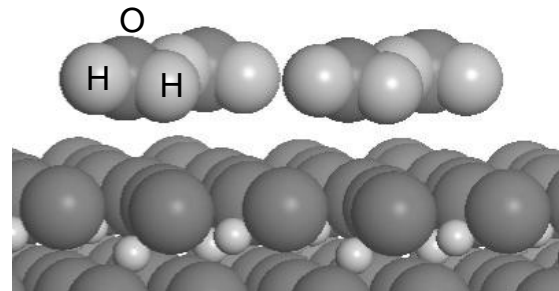
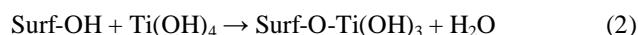


Fig. 4 The hydrated (004) surface of Cr_2O_3 .

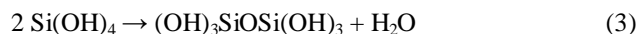
In the case of Cr_2O_3 surfaces, there is no consistent understanding of the adsorption mechanism of water. According to the experimental studies (Cappus et al., 1993; Maurice et al., 2001; Henderson et al., 2000; Henderson, 2002), water dissociates both on the Cr_2O_3 surfaces and in the bulk structure. On the other hand, the theoretical study estimates that the adsorption of water molecules is more favourable than their dissociation (Bredow, 1998). Because a generally accepted mechanism for the adsorption of water does not exist, the adsorption studies were computationally performed in this study. Three different possibilities were taken into account: molecular adsorption, dissociative adsorption, and partly molecular and partly dissociative adsorption. Adsorption mechanisms were investigated on three different surfaces: (10-2), (006) and (004). The investigation indicated that the (004) surface is the only one where water forms an energetically stable hydrated surface (Fig. 4). On the other surfaces, the adsorbed water molecules dissociate, and at the same time, the converse reaction produces water. Therefore, the dissociative adsorption is also possible on the Cr_2O_3 surfaces, but it is not the predominant phenomenon on the investigated surfaces. On the hydrated (004) surface, water is in a

molecular form, and adsorption is physical. The adsorption energy is only -0.06 eV. Based on these findings, the formation of salt depositions was investigated only on the non-hydroxylated Cr_2O_3 surfaces.

On the rutile surfaces, our aim was to clarify differences in the fouling chemistry of titanium and silicon compounds. Based on our earlier analysis of the depositions (Puhakka et al., 2007) and proposed reactions (Santacesaria et al., 1986; Iler, 1979), olation and oxolation reactions of titanium hydroxyls and silanols were the interesting ones. In order to simplify the comparison of chemistry of compounds, neutral $\text{Ti}(\text{OH})_4$ and $\text{Si}(\text{OH})_4$ compounds were used as models for the species causing fouling. The reaction path from reactants to products was determined by transition state calculations. Especially, our interest was on the condensation reaction between the heat transfer surface and foulant. For example, the reaction between the hydroxylated rutile surface and $\text{Ti}(\text{OH})_4$ can be described with the following reaction:

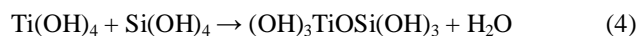


Our study (Puhakka et al., 2007) indicated that a single $\text{Ti}(\text{OH})_4$ molecule can react in ideal conditions with the hydroxyl group of TiO_2 surface (-9.72 kJ/mol) according to the reaction 2, but the reaction of a single $\text{Si}(\text{OH})_4$ molecule is strongly endothermic (68.24 kJ/mol). Although $\text{Si}(\text{OH})_4$ molecules do not react with the hydroxylated rutile surface, they react with each other via condensation reaction (Terry, 1983):



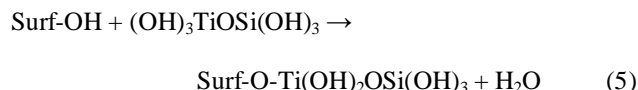
The energy released in this exothermic reaction is -48.28 kJ/mol. On the other hand, the reaction for two $\text{Ti}(\text{OH})_4$ is not favourable (45.12 kJ/mol).

In this study, we continued to investigate the condensation reaction mechanism between titanium hydroxyls and silanols according to the reaction:



It was realized that the reaction between $\text{Ti}(\text{OH})_4$ and $\text{Si}(\text{OH})_4$ also takes place via condensation reaction. The energy of the reaction is -50.36 kJ/mol, and products are $(\text{OH})_3\text{TiOSi}(\text{OH})_3$ species and a water molecule (Fig. 5). Based on these results, titanium compounds can react via their hydroxyl groups with the hydroxylated titanium dioxide surface and form chemical bonding with the heat transfer surface. Therefore, titanium depositions are very difficult to clean up. Cleaning of the silicon deposited surfaces is less laborious, because the silanol compounds form polymeric silicon species which are only hydrogen bonded on the surface. When the deposition contains both the titanium and silicon compounds, it is possible that the

titanium part with hydroxyl groups reacts with the hydroxylated surface according to the condensation reaction:



Then, the titanium part can act as an adhesive in fouling reaction. This assumption is based on the surface condensation reaction which was predicted to happen between the hydroxylated rutile surface and $\text{Ti}(\text{OH})_4$. Then, a chemical reaction happens between the surface and the foulant molecule, and at the same time, the water molecule release. The reaction can also be called for a dehydration reaction. The reaction is possible only, if there are hydroxyl groups on the surface. The formation of hydroxyl groups depends on vacant cation sites.

The calculated results are consistent with our analysis of the depositions (Puhakka et al., 2007), which indicated that fouling during the crystallization process of TiO_2 is caused by amorphous silica and poorly crystalline titanium salts. Silica is only a trace element in the process fluid but is found in larger amounts from the depositions on the heat exchanger surfaces.

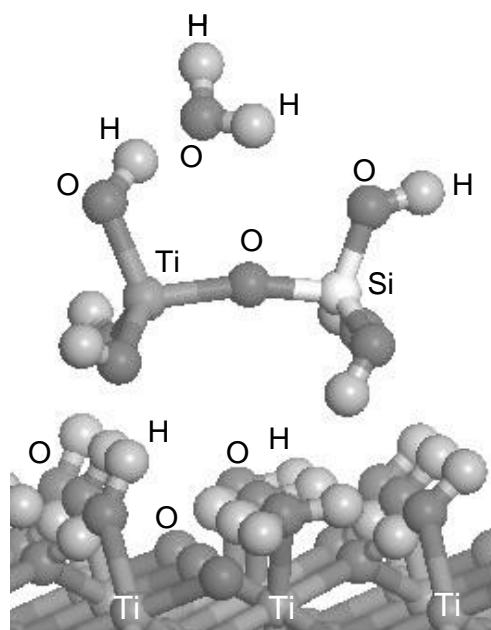


Fig. 5 The $(\text{OH})_3\text{TiOSi}(\text{OH})_3$ species: the product of condensation reaction of $\text{Ti}(\text{OH})_4$ and $\text{Si}(\text{OH})_4$.

On the non-hydroxylated Cr_2O_3 surfaces, the water-soluble depositions of different ions were investigated. Especially, the role of cations and anions in the initial phase

of fouling was interesting. The investigated cations were sodium (Na^+), potassium (K^+), and calcium (Ca^{2+}), and anions were carbonate (CO_3^{2-}) and sulphate (SO_4^{2-}). Adsorption studies were performed for both the fully oxidated Cr_2O_2 surface, (004), and the partially oxidated Cr_2O_2 surfaces, (10-2) and (006). First, the adsorption positions of cations and anions were determined on different surfaces, and based on those structures, the adsorption energies were calculated (Table 1). The results indicate that cations adsorb strongly onto Cr_2O_3 surfaces, but anions repel clean surfaces. It is most probable that the surface charge density of the Cr_2O_3 favours the formation of the partly covalent type bonding between the surface and cations (Fig. 6a). For example, the adsorbed Ca^{2+} ion is bound to three surface oxygens.

Table 1. Calculated adsorption energies of cations and anions on the Cr_2O_3 surfaces.

	Surface	Adsorption energy ΔE (eV)
H_2O	(004)	-0.06
Ca^{2+}	(004)	-9.91
Ca^{2+}	(10-2)	-8.26
Na^+	(10-2)	-4.92
K^+	(004)	-5.01
K^+	(10-2)	-3.84
SO_4^{2-}	(006)	8.62
CO_3^{2-}	(10-2)	8.40
CaSO_4	(10-2)	-3.40
CaCO_3	(10-2)	-3.00

Although the repulsion between the Cr_2O_3 surfaces and anions was detected, the salt depositions are known to form onto the stainless steel surfaces. Therefore, the adsorption of anions, carbonate and sulphate were investigated on the surface where the calcium cations are present. Then, anions reach the energetically stable positions from short range of cations, and ionic compounds, calcium carbonate and calcium sulphate are formed. This is in consistence with the understanding that the adsorption of the cations changes the surface charge densities (Fig. 6b). Thus the coordination of anions onto the Cr_2O_3 surfaces is possible. Based on this, the adsorption of cations (inner-sphere complexes) and chemical bonding with the surface oxygens on the clean surface are favoured, which causes that electron densities are concentrated around the cations. Because of this the repulsion force of the surface against anions (outer-sphere complexes) decreases, and the adsorption of the anions is possible. After that the atomic ordering of ion pairs takes

place, and a crystal lattice of deposition occurs layer by layer on the surface.

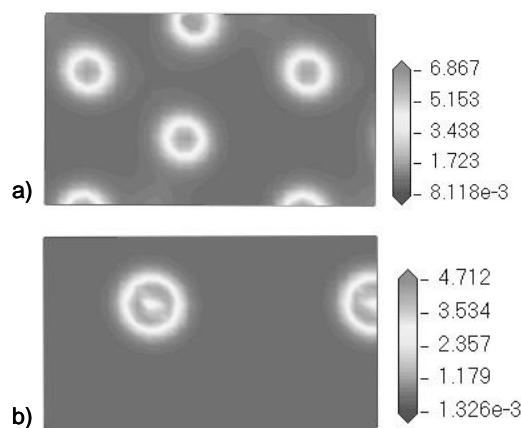


Fig. 6 Surface charge densities presented as electrons in $1 \cdot 10^{-30} \text{ m}^3$. a) The (004) surface of Cr_2O_3 . b) The Ca^{2+} adsorbed onto the (004) surface of Cr_2O_3 .

CONCLUSIONS

The present study indicated that different fouling mechanism on heat transfer surfaces can be distinguished by using molecular modelling techniques. Molecular modelling is capable to estimate the significance of the chemical effects of process fluid on the uppermost layer structure of the heat transfer surface: its electron densities and thus the reactivity of the passive oxide layer and the state of adsorbed water. The study indicated that the dissociation of water is not favourable on the Cr_2O_3 surfaces unlike it was predicted in the earlier theoretical studies (Goniakowski and Gillan, 1996; Lindan et al., 1996; Langel, 2002; Diebold, 2003; Menetrey et al., 2003) for the TiO_2 surfaces. Therefore, on the Cr_2O_3 surfaces, fouling depends on the changes in electron densities of the surface, whereas on the TiO_2 surfaces, the surface hydroxyl groups originated from the dissociation of water control the fouling reactions. It was noticed that condensation reactions of titanium hydroxyls and silanols are favourable on the hydroxylated surface, and then foulants can react via their hydroxyl groups with the surface and form chemical bonding with the heat transfer surface. On the non-hydroxylated surfaces, chemical reaction by adsorption of cations onto the surface and the ion pair formation with anions is the predominant fouling mechanism.

ACKNOWLEDGEMENTS

This work was financially supported by Tekes, the Finnish Funding Agency for Technology and Innovation, and industrial partners.

NOMENCLATURE

BFDH	Bravais-Friedel Donnay-Harker method
CASTEP	CAMbridge Serial Total Energy Package
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
GGA-PW91	Generalized Gradient Approximation (Perdew-Wang)
L	Ligand
Surf	Surface

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