

MOLECULAR MODELLING APPROACH ON FOULING OF THE PLATE HEAT EXCHANGER: TITANIUM HYDROXYLS, SILANOLS AND SULPHATES ON TiO₂ SURFACES

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ABSTRACT

Molecular modelling is a novel approach in the field of fouling research. Method was used to calculate fouling reactions and molecular level interactions between heat transfer surface and flowing fluid. The focus was on the comparison of reaction mechanism of Ti(OH)₄ and that of Si(OH)₄ on rutile (101) surface. The calculated reaction energies indicate strong chemical bonding via condensation reaction of titanium(IV) hydroxyls and weak hydrogen bonding of silanols without chemical reaction on the surface. Chemical composition and structural properties of fouling layers from real process were characterized. On the heat transfer surfaces, deposits containing titanium had dense structure and were very difficult to clean while silica was porous and amorphous causing less severe problems in cleaning. Molecular modelling was found to be an effective tool in predicting reaction mechanisms and interaction forces between the fouling fluid and heat transfer surface at molecular level.

INTRODUCTION

Molecular modelling has 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 calculation power rather complex cluster or periodic model systems can be calculated (Goniakowski et al., 1996; Ahdjoudj et al., 1999; Lindan et al., 1996; Langel, 2002; Diebold, 2003; Menetrey et al., 2003), which enables even practical engineering problems to be solved. In this study we have applied it in the field of fouling research. The advance of the method is to define mechanistic kinetic routes which may not be defined from process measurements and fouling resistance curves. The aim of the molecular modelling work was to clarify, if there is any chemical explanation at molecular level for the fouling of titanium heat exchangers in titanium dioxide production by the sulphate process route.

Chemistry of titanium

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, rutile and anatase are the most important ones in the applications of TiO₂. Though, the heat exchangers are manufactured from titanium metal, the outermost layer of metal is spontaneously covered by a surface oxide layer, TiO₂ (Sul et al., 2001). The oxide layer on the titanium surface gives excellent resistance against corrosion for titanium materials (Leng et al., 2004). 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 Ti can be considered as rutile.

In aqueous solutions of sulfuric acid, titanium(IV) can exist in many hydrated forms, which can be presented with formula Ti(OH)_x^{(4-x)+}; x < 4 (Comba and Merbach, 1987; Sugimoto et al., 2002). Strong complexation of titanium with SO₄²⁻ is known (Beukenkamp and Herrington, 1959) as well other complexes of form [Ti(OH)_nL_m]^{(4-n-m)+} are reported. Olation and oxolation reactions, where multinuclear polymeric species are formed are typical in concentrated titanium solutions. This reaction is referred also condensation polymerization, because this reaction mechanism produces water molecules when oxo-bridge -O- or olo-bridge -OH- is formed between Ti atoms. Sulfate bridge -SO₄- is proposed to be the result of partial depolymerisation and this will favour definite molecular orientation during precipitation, namely anatase structure (Santacesaria et al., 1985).

Solid phases precipitated from aqueous sulfuric acid solutions are hydrous oxides and sulfates (Barksdale, 1966; Jalava et al., 2000). Solubility isotherms predict five sulfates (Belokoskov, 1962) of which TiOSO₄·H₂O and TiOSO₄·2H₂O have been characterized by their crystalline structure (Gatehouse and Platts, 1993).

Chemistry of silica

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, number of siloxane $-\text{Si-O-Si}-$ is formed. This will result in an amorphous silica precipitate (Terry, 1983).

Process description

The plate heat exchangers (PHEs), construction material of which is metallic titanium, are used as a pre-heater in the crystallization process of TiO_2 pigment. The precipitate liquor from storage tank is pumped to the crystallizer and at the same time heated. The precipitate liquor, which causes the fouling, consists of three main elements (Jalava, 1992): sulfuric acid (430 g/dm^3), soluble titanium (228 g/dm^3) and iron (114 g/dm^3). Concentrations of trace elements depend strongly on the quality of used ilmenite ore. Fouling of PHEs is so severe that they have to be opened for cleaning sometimes even once a month.

METHODS

Analysis of depositions

The elemental composition of deposits was analysed from solid sample with semiquantitative X-ray fluorescence (XRF) spectrometer and UNIQUNT4 software. Inductively coupled plasma (ICP) analyser Perkin Elmer 4300 DVC was used as a reference analysis method. Crystal structure of the depositions was determined with X-ray powder diffraction (XRD) using an angle-dispersive Philips PW 1820 analyser and nickel-filtered copper $K\alpha$ radiation. Scanning Electron Microscopy with Energy Dispersive Spectrum (SEM-EDS) was used to determine the surface morphology.

Thermodynamic calculations

OLI Systems Inc. (Brattli, 2001) model was used in estimating the equilibrium distribution of aqueous species in the studied system. The OLI Engine is a commercial simulation package which models aqueous systems with modified Pitzer model, which is used for representing solution non-ideality (Rafal et al., 2005). Thermodynamic

modelling of aqueous electrolytes gives possibility to estimate the equilibrium species of the electrolytes in defined system. For the basis of the calculations thermodynamic data (ΔH , ΔS , $C_p(T)$), activity coefficient model for non-ideal or concentrated solutions and a computer for calculations are needed.

Molecular modelling

Molecular modelling methods were used to investigate the crystal and surface structures of rutile, and the adsorption mechanism of $\text{Ti}(\text{OH})_4$ and $\text{Si}(\text{OH})_4$ on the rutile (101) surface. Calculations was done utilizing Cerius² version 4.6 (Accelrys, 2001) and Materials Studio versions 3.0 (Accelrys, 2003) and 3.1 (Accelrys, 2004) softwares. *Ab initio* quantum mechanics calculations were performed with the CASTEP code. The exchange-correlation was described with generalized gradient approximation, GGA-PW91, during the geometry optimization of the crystal and surface structures. For each element, ultrasoft pseudopotentials were used. In the potential of titanium, 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. The morphology of rutile was predicted by using the Bravais-Friedel Donnay-Harker (BFDH) method implemented into the Cerius² 4.6 version. In the reaction path calculations, the exchange-correlation potential was GGA-PBE.

RESULTS AND DISCUSSION

The flow arrangement in the stages of the heat exchanger (Fig. 1) gave an opportunity to take samples from different temperature regions. Sampling was done when the heat exchanger was opened for cleaning. Three consecutive fouling periods were analyzed.

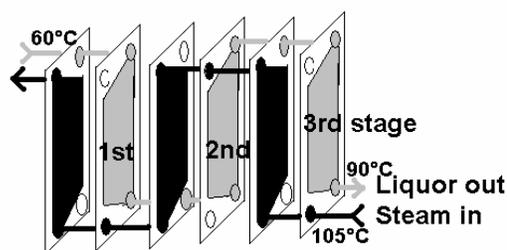


Fig. 1 Schematic presentation of the staged plate heat exchanger and its flow arrangements.

Deposition analyses indicated that the fouling 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 depositions on heat exchanger surfaces.

The amount and structure of the deposition strongly depended on the position inside the PHE. Titanium content increased and silica decreased along the flow path when

increasing temperature (Fig. 2). Sulphate content remained nearly constant. Deposited mass per area and its density, thickness and crystallinity increased when increasing temperature.

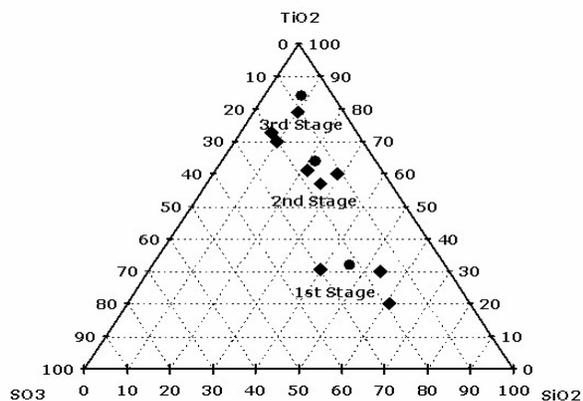


Fig. 2 Composition of the depositions, analysis done with XRF (◆) and reference analysis with ICP (●) at different temperature regions.

XRD shows (Fig. 3) that at lower temperatures, at stage 1, the deposition was mainly amorphous. Weak peaks of anatase and silica as quartz were found. Crystallinity of anatase increases with increasing temperatures at stage 2 and stage 3 while peak of silica disappears. Crystal size determined by XRD for anatase was only 16 nm which indicates that also at stage 3 the deposition is poorly crystallized.

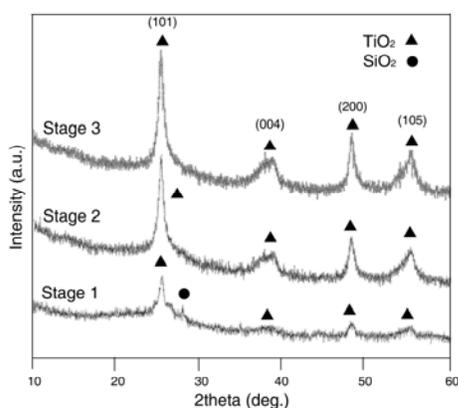


Fig. 3 XRD-spectrum from the depositions formed on the heat transfer surfaces at different temperature regions.

SEM analysis was done for the samples from all three stages. At lower temperatures (Fig. 4), the deposit structure was highly porous and has network structure typical for silica.

At higher temperatures, porosity decreases and more dense agglomerates can be observed. Fig. 5 presents the agglomerate for anatase-like structure which is formed from ellipsoidal dense crystals. According to SEM analysis the colloidal size particles can be observed. For the better understanding of the growth of deposition layer, colloidal forces may also need to be treated.

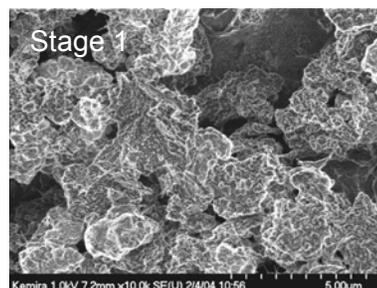


Fig. 4 SEM image of the deposit formed in the lower temperatures at stage 1 in the PHE.

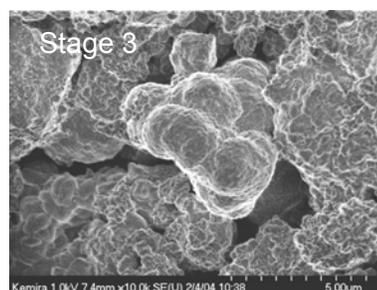


Fig. 5 SEM image of the deposit formed in the higher temperatures at stage 3 in the PHE.

The thermodynamic model of soluble titanium species in weak solutions (Fig. 6a and 6b) have quite similar speciation of soluble species with Baes and Mesmer (1976) and in concentrated solutions (Fig. 6c) with the results of Beukenkamp and Herrington (1960). The calculated main species in the weak sulphuric acid solution is neutral soluble titanium species $Ti(OH)_4$ and in concentrated solutions $TiOSO_4$ which were indicated by $Ti(OH)_3HSO_4$. Higher temperatures (Fig. 6b) favours neutral species to be formed compared with the room temperature results (Fig. 6a). However, Santacesaria et al. (1986) indicate that titanium(IV) forms multinuclear species. The accuracy of the model does not allow to calculate solubilities of solid phases for titanium and lack of thermodynamic data does not allow to calculate the speciation equilibrium of multinuclear soluble species.

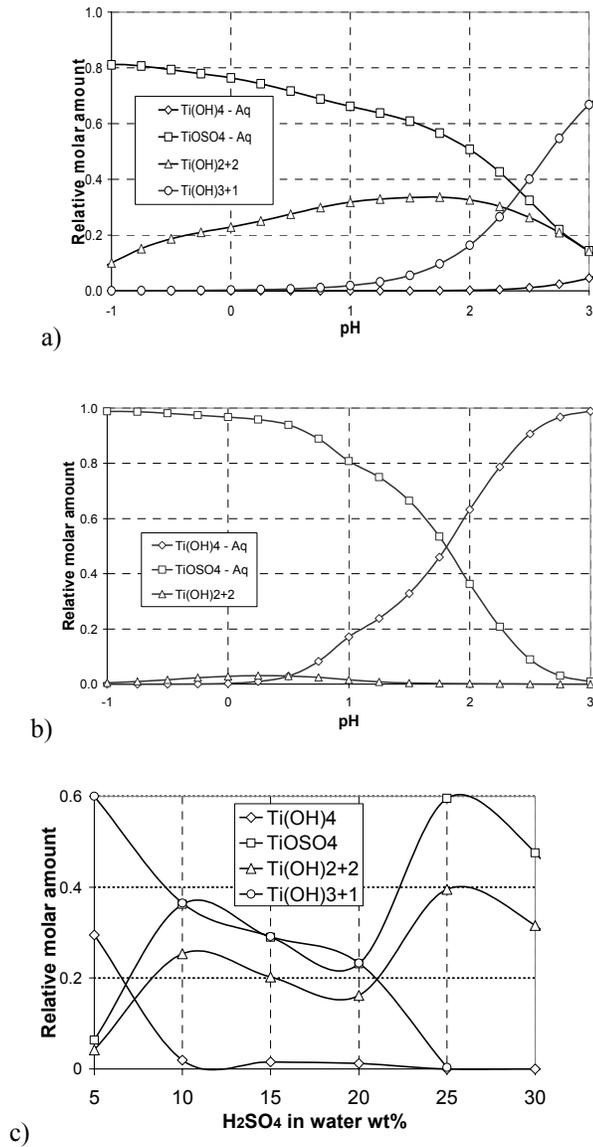


Fig. 6 Relative molar amounts of titanium complexes in weak aqueous sulphuric acid solution in pH scale a) at 25°C and b) at 90°C and c) in concentrated solutions vs. sulphuric acid concentration at 90°C.

In the molecular modelling studies, the oxide layer structure of clean heat transfer surface was supposed to consist of thermodynamically stable rutile structure. Therefore, the starting point for the modelling studies was the tetragonal rutile lattice ($a = b = 459.4$ pm, $c = 295.9$ pm and $c/a = 0.644$) with symmetry $P4_2/mnm$ (Accelrys, 2001). The lattice parameters of the optimized structure are $a = b = 470.2$ pm, $c = 301.7$ pm and $c/a = 0.642$. Based on the optimized rutile structure, the morphology of rutile was

predicted by the BFDH method (Fig. 7). There are two dominant plane surfaces: (110) and (101). The estimated surface area of the (110) surface is 59.4 % and that of (101) surface is 40.6 %. The structure of edge sites corresponds the (111) surface.

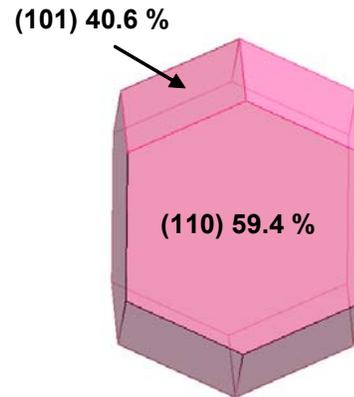


Fig. 7 Estimated morphology of rutile by BFDH method.

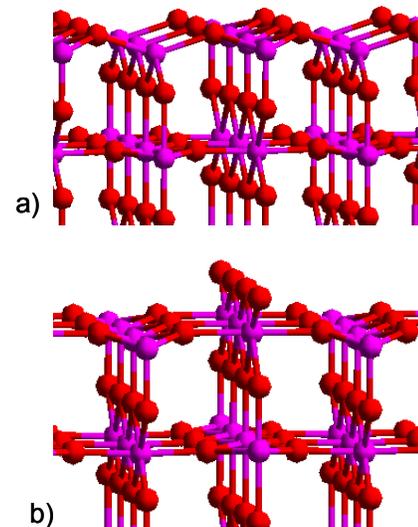


Fig. 8 The (110) surface of rutile with a) four- and five-coordinated and b) five- and six-coordinated titanium atoms.

On the (110) surface cleaved from the rutile lattice, the titanium atoms are four- or five-coordinated (Fig. 8a). The surface is generally presented in the so-called auto-compensated form (Fig. 8b) where the same number of Ti-O and O-Ti bonds are broken (Diebold, 2003). In this case, the titanium atoms are five- or six-coordinated, and there are bridge oxygen atoms on the surface. Respectively, on the (101) surface, the titanium atoms are three-coordinated (Fig. 9a), but on the auto-compensated surface, the coordination number of titanium atoms is five (Fig. 9b).

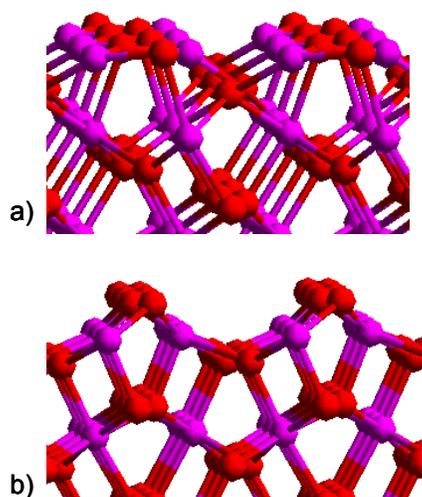


Fig. 9 The (101) surface of rutile with a) three-coordinated and b) five-coordinated titanium atoms.

Table 1. Surface atom relaxations of rutile compared to its bulk structure.

| Surface | Spacing X ^a – Ti ^b | d ^c (%) |
|-----------------------|--|--------------------|
| (110) | 4-coord. Ti – Ti | -0.2 |
| | 5-coord. Ti – Ti | +1.0 |
| | 3-coord. O – Ti | +17.6 |
| (110) autocompensated | 5-coord. Ti – Ti | -2.7 |
| | 6-coord. Ti – Ti | +10.3 |
| | 3-coord. O – Ti | +8.6 |
| (101) | bridge-O – Ti | -2.3 |
| | 3-coord. Ti – Ti | -19.8 |
| | 3-coord. O – Ti | +8.1 |
| (101) autocompensated | 5-coord. Ti – Ti | -3.8 |
| | 2-coord. O – Ti | -1.7 |
| | 3-coord. O – Ti | +1.1 |

^a An X atom is on a surface layer.

^b A six-coordinated titanium atom on the second layer.

^c Difference between atomic layers.

In order to get a more profound description of the sterical and electrostatic factors of the rutile surfaces, reconstruction of the surface atom layers was taken into account. Comparison of the changes in the atomic layer spacing indicates that the changes on the (110) surface are more significant than on the (101) surface. The changes in the atomic layer spacing are presented in Table 1. Based on this result, the autocompensated (101) surface was chosen to be the model structure for heat transfer surfaces.

In the process conditions, clean heat transfer surfaces described by the rutile structure are affected by species in process liquor. The most important adsorbate is water. According to the literature (Goniakowski et al., 1996; Lindan et al., 1996; Langel, 2002; Diebold, 2003; Menetrey et al., 2003), most theoretical studies predict that water adsorbs onto the (100) and (110) rutile surfaces dissociatively. Based on these results, we have supposed that adsorption of water is also similar on the auto-compensated (101) surface where all titanium atoms are five-coordinated. Therefore, the TiO₂ surface was covered by hydroxyl groups, and the surface structure was allowed to relax in order to receive the stable hydroxylated surface for our fouling reaction mechanism studies.

Based on our analysis of the depositions and proposed reactions (Santacesaria et al., 1986; Iler, 1979), we focused on olation and oxolation reactions of titanium hydroxyls and silanols in our reaction mechanism studies. The aim of our study was to clarify differences in the fouling chemistry of titanium and silicon compounds. Therefore, we have used neutral Ti(OH)₄ and Si(OH)₄ compounds as models for the species causing fouling. The reaction path from reactants to products was determined by transition state calculation. According to thermodynamic analysis, the soluble species, Ti(OH)₄, was used in molecular modelling to calculate the interactions and reactions between the process fluid and heat transfer surface. This species was expected to explain the kinetic mechanism of oxolation and olation reactions generally. A chain structure of Ti-O chain referred as (TiO)_n²ⁿ⁺ is so rigid, that in calculations the thermodynamic motion of the chain should be taken into account. Therefore, the effect of (TiO)_n²ⁿ⁺ and other multinuclear soluble species for fouling was not used in our calculations.

For silicon neutral compound, Si(OH)₄ comparable to titanium species was selected as a fouling compound in the modelling. However, a weak solution complex of composition [Si(OH)·SO₄²⁻] is suggested (Marshall et al., 1982) to explain SiO₂ enhanced solubility above 150 °C in Na₂SO₄ solutions. Optimized molecular structures were able to be defined for sulphate bridges between Si atoms and Si and Ti atom but not between two Ti atoms.

Transition state calculations indicated that a single Ti(OH)₄ molecule can react in ideal conditions with the hydroxyl group of TiO₂ surface (-9.72 kJ/mol). The coordination geometry of Ti(OH)₄ corresponds the structure of anatase (Fig. 10a), so the result is consistent with our deposition analysis, the titanium depositions form anatase-like dense crystals. At the same time, the reaction of a single Si(OH)₄ molecule is strongly endothermic (68.24 kJ/mol) with the hydroxylated surface.

When the coverage of Ti(OH)₄ increases on the rutile (101) surface, the hydroxylated surface changes to surface, where only one half of hydroxyl groups remains and one half of them produces water molecules adsorbed onto the

surface. This finding is consistent with earlier theoretical results (Goniakowski et al., 1996; Diebold, 2003; Menetrey et al., 2003). Above this new surface, two $\text{Si}(\text{OH})_4$ molecules react via condensation reaction (Terry, 1983). In this exothermic reaction (-48.28 kJ/mol), $(\text{OH})_3\text{SiOSi}(\text{OH})_3$ species and water molecule are formed (Fig. 10b). On the other hand, the reaction for two $\text{Ti}(\text{OH})_4$ is not favourable (45.12 kJ/mol). This indicates that weakly hydrogen bonded $\text{Si}(\text{OH})_4$ forms amorphous depositions on the heat transfer surfaces like our deposition analysis revealed.

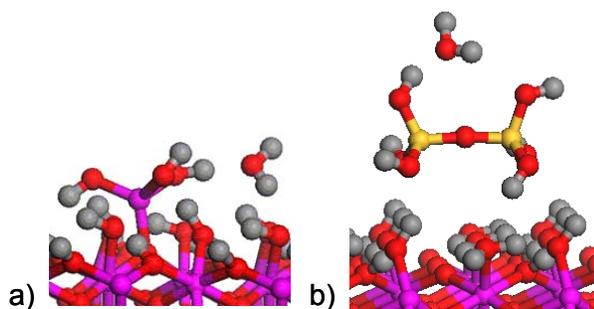


Fig. 10 Condensation reactions: a) formation of a $\text{Ti}(\text{OH})_3$ group on the hydroxylated rutile (101) surface and b) formation of $(\text{OH})_3\text{SiOSi}(\text{OH})_3$ species on the half-hydroxylated rutile (101).

In the further studies, soluble titanium-sulfate complex as TiOSO_4 should be considered in calculations as well as possibility to use the $\text{Ti}(\text{OH})_2^{2+}$ ion. The results of these would be beneficial comparing the energies of reactions presented in this paper.

Molecular modelling methods used have treated fouling with molecular level interactions between hydroxylated rutile (101) surface and fluid. There is an evidence of polymeric species and colloidal particles to be present in the titanium and silicon solution, in this study we have not considered colloidal forces between particles and their attachment on surface. To model fouling process taking into account larger elements than atoms, a different approach than molecular modelling needs to be used.

CONCLUSIONS

The present study demonstrated that the new molecular level insight into fouling can be received by using molecular modelling techniques. According to our studies, condensation reactions of titanium hydroxyls and silanols on the heat exchanger surfaces are involved in the fouling of the preheater in the crystallization process of TiO_2 pigment. In addition and together with aggregate formation in solution and attachment of colloidal particles on surface, titanium compounds can react via their hydroxyl groups with the hydroxylated surface and form chemical bonding with the heat transfer surface. The deposited titanium has

the crystalline structure of anatase. Silanols react with each others above the surface forming polymeric silicon species which are hydrogen bonded on the surface. The deposited silica has an amorphous structure.

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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-PW91 | Generalized Gradient Approximation (Perdew-Wang) |
| ICP | Inductively Coupled Plasma |
| L | Ligand |
| PHE | Plate Heat Exchanger |
| SEM-EDS | Scanning Electron Microscopy with Energy Dispersive Spectrum |
| XRD | X-Ray Diffraction |
| XRF | X-Ray Fluorescence |

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