CONTROLLING OF PARTICLE INTERACTIONS WITH PROCESS PIPES IN CALCITE MINERAL PROCESSING TO PREVENT DEPOSITIONS

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Introduction

Depositions formed by fouling on the process equipment are still a common problem in almost all industrial fields. To overcome the fouling, either by preventing or cleaning, generally leads to additional operation, maintenance and capital costs and that affects the profitability of the whole process. Deposition of crystals on heat transfer surfaces is common in aqueous systems where solutions are evaporated and heated. [1] Other fouling mechanism is deposition of particulate material. Adhesion is an important step in the accumulation of inorganic particles, macromolecules and micro organisms on heat exchanger surfaces. Because the size of such material is less than 1 μ m, interactions are described in terms of colloid chemistry. [2]

An evaporation train in a mineral grinding process has problematic fouling caused by silicates and calcite. Previous thermodynamic calculations have been used to present phase and chemical equilibrium in the case of crystallization fouling for an evaporation process. [3] Another recognized fouling mechanism in the process is deposition of particles. In this report the studies on colloidal interactions with particle and surface is presented.

Colloidal interactions - Extended DLVO theory

Process fluids contain often solid particles that can deposit on the heat transfer surfaces. Particle attachment is affected by surface forces and by hydrodynamic forces near the surface. The adhesion of the colloidal particles ($10 \text{ nm} - 10 \mu \text{m}$) on a surface are controlled by Lifshitz - Van der Waals interaction forces (LW), Electrostatic double layer interaction forces (EL), Lewis acid-base interactions (AB) and Brownian motion (Br) [4]. In terms of energies the total interaction energy can be written as a sum of the four interaction terms given:

$$\Delta G^{TOT} = \Delta G^{LW} + \Delta G^{EL} + \Delta G^{AB} + \Delta G^{Br}$$
⁽¹⁾

Adhesion of the particles on the surface 'fouling' takes place under those conditions where ΔG^{TOT} is negative. To obtain individual contributions to the total interaction energy calculated, experimental contact angle and ζ -potential data are required.

Experimental

Particle size distribution was determined with Beckman Coulter LS 13 320. Based on mass concentrations, particle populations of $0.36 \,\mu$ m and $2.0 \,\mu$ m were found and based on number concentrations. Comparable sizes of particles were identified in electron microscopy analysis.

The elemental composition of pigment feed and depositions from surfaces of the process were analyzed with SEM-EDS. The amount of impurities was lower than 1 wt-% in the pigment feed but in the depositions of the process units the amount of silicon and manganese were 2–9 wt-% and 1–6 wt-%, respectively.

 ζ -potential of calcite pigment particles were measured with Coulter® Delsa 440SX in order to obtain EL interactions. To adjust pH, analytical grade 0.1 M NaOH and HNO₃ (J.T. Baker) were used. In **Fig. 1**, ζ -potential of a calcite pigment is negative and almost constant at pH range from 6.5 to 12. ζ -potential was not measured at lower pH values (<6.5), because in acidic conditions calcite solubility increases markedly.



Fig.1. ζ -potential of a calcite pigment.

A diverse behavior of ζ -potential values of calcite particles has been reported. Vdovic [5] (2000) explains that natural calcite minerals are negative and independent of pH and synthetic calcite values are positive having biggest value at pH 8.4.

 ζ -potentials for Stainless Steel AISI 316L were derived from streaming potential measurements [6]. The point of zero charge (pzc) varies between pH 3-5 depending on the cleaning agent and surface topography. Steel surface and calcite particles are both negative and thus have repulsive electrostatic interaction.

Particle (SiO₂,CaCO₃, talc and dolomite) surface energies used in calculations, were determined with the Thin layer wicking [7] and untreated steel surface AISI316L_2B and coated steel surface energies were determined [8] with the Sessile drop method.

Results and discussion

Fouling, *i.e.* particle attachment on a surface, is thermodynamically favored when ΔG^{TOT} is negative at the equilibrium distance (when the contact of particle and wall distance is around 2 nm). Even then, colloidal stability can hinder fouling markedly, which is a result of local maximum in the energy *vs.* distance diagram. In **Fig. 2a** between SiO₂ particle and untreated Steel AISI 316L in the conditions of a calcite pigment process an energy barrier (local maximum) occurs that hinders fouling. However, gradual fouling must take place, due to the strong primary minimum of attraction.

A secondary maximum higher than 10 kT should prevent particle attachment for a long period of time, but for smaller particles in the same environment this is lower and do not prevent them on attachment. Means to affect the secondary maximum are to decrease ionic strength or to change particle and surface ζ -potentials.

Usually in industrial processes, ionic strengths are much higher than 0.1 mol/l, when electrostatic interactions have only very small contribution on total interaction. In the case of fouling, the best situation would be when no primary minimum occurs. This can be achieved by modifying surface material. In **Fig. 2b** Lewis acid-base interactions are repulsive with SiO_xCVD coating and primary minimum in total interaction energy does not occur. Particle attachment should be prevented; in this case, two highly hydrophilic bodies are repulsive.



Fig. 2. Energy *vs.* distance diagram between SiO₂ particle (200 nm) and **(a)** AISI 316L steel illustrating metastable situation, where weak colloidal stability occurs, **(b)** SiO_xCVD coated steel where Levis acid-base interactions (AB) are repulsive.

The dependence of particle chemical composition on adhesion was calculated for the main minerals and impurities in calcite pigment process. In Table 1 adhesion of pure calcite on Steel AISI 316L surface is much weaker compared to magnesium containing mineral dolomite $CaMg(CO_3)_2$. Adhesion increases with talc $MgSiO_2$ and SiO_2 , but is strongest with gypsum $CaSO_4$. Compared to the concentration of magnesium and silicon in the calcite pigment and in the depositions on the surfaces, depositions have much higher amounts of those. This is due to stronger adhesion of magnesium and silicon containing particles on steel surface than with pure calcite.

Table 1. Effect of particle composition on adhesion on steel AISI 316L	surface in the
conditions of calcite pigment process.	

Particle	ΔG ^{τοτ} /kT
composition	
CaCO ₃	-6,4
CaMg(CO ₃) ₂	-32,2
SiO ₂	-34,8
MgSiO ₂	-52,3
CaSO ₄	-119,6

In **Table 2** effect of surface material on adhesion is shown with SiO_2 particles in the calcite pigment process conditions. With the studied coatings Titanium nitrile has the smallest adhesion on particles. Thus, titanium as a construction material is better than untreated and most of coated steels.

Surface material	ΔG ^{TOT} /kT
TiN	28,6
SiO _x PECVD	25,3
Titanium untreated	8,7
SIF_3^+	-5,7
SiO ₂ Sol-gel	-21,6
MoS_2^{2+}	-26,8
AISI 316L 2B steel	-35,6

 Table 2. Effect of surface material and coating on adhesion of SiO₂ particles.

Adhesion energy between particle and surface in **Fig. 3** was almost linearly dependent on the negative Levis acid-base (AB-) component of surface tension. The total surface tension of coatings varied markedly, but could not explain differences between adhesion energies.



Fig. 3. Dependency of adhesion energy on surface tension between SiO₂ particle and different surface materials.

In the case of crystallization fouling low energy surfaces are less prone to foul. To prevent fouling with modifying surface energies is a challenge because different surface properties are needed in affecting crystallization and particle attachment, which can be conflicting.

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