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Development of a swelling-removal model for the scanning fluid dynamic gauge



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ABSTRACT

A mathematical mechanistic swelling-removal approach has been developed for modelling the cleaning process in dried protein samples using the scanning fluid dynamic gauge (sFDG). The algorithm combines swelling phenomena with removal mechanisms (shear stress removal and soil dissolution). Swelling phenomena were described by applying analytical expressions based on poroelasticity theory. The nonlinear partial differential equation (PDE) describing the thickness swelling ratio was solved numerically, allowing the soil to be divided into theoretical layers. The novelty is presented as the cleaning process is integrated by the elimination of those layers. The model predicts the variation of the soil thickness over time. To describe kinetics of removal, experimental results were considered. Constant removal rates were found after an initial transition period. Removal rates were dependent on the different chemical and physical factors acting: temperature, chemistry concentration (pH, enzyme level), shear stress and frequency of application of shear stress. Soil remaining, total mass or percentage of cleaning over time can also be calculated as outputs. Overall the model has the potential to apply varying cleaning conditions over time and grow to a more theoretical approach in the future by applying enzyme kinetics.

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1. Introduction

To remove soft soil deposits off a hard surface it is necessary to overcome the cohesive forces that bind the soil together and the adhesive forces that bind the soil to the substrate. Factors affecting the effectiveness of the removal range from the nature and state of the soil to physical and chemical factors such as flow rate (shear stress applied), concentration of chemicals (pH, enzymes) or temperature (Wilson, 2005).

Fryer and Asteriadou (2009) proposed a classification for cleaning phenomena based on types of soils and mechanisms of removal. Soils were classified based on their physical properties, ranging from *low viscosity fluids* to *cohesive solids*. Cleaning fluids were classified from *water at ambient* to *hot chemicals*. The cleaning mechanism occurring varies depending on the case given: a *fluid mechanic removal* happens when the shear stress imposed by the flow of a fluid over the soil is large enough and no chemicals are needed. However, a *diffusion-reaction removal* involves the presence of chemicals. Different dynamic processes might occur in parallel, involving mass transfer from the bulk of wash solution to the soil, a subsequent diffusion of the actives species, the change of the soil inner properties due to chemical reactions and the increase in moisture content (phase changes). This leads to a weakening of the soil structure that facilitates the cleaning process. Once the soil molecules are disengaged, a reverse mass transfer phenomena occurs. Released particles must travel to the boundary soil-wash solution layer and then be completely removed. The rate limiting stage controls the total removal time.

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Nomenclature		
	D _{eff}	effective diffusion coefficient
	Ea	activation energy
	f	frequency function. Step function (0 or 1)
	h(t)	total sample thickness at time 't'
	Н	layer thickness in the dry state
	Jz	diffusion flux
	k	constant incorporating characteristics of
		macromolecule and penetrant system
	k _{ds}	removal rate by soil dissolution
	k _{ss}	removal rate by shear stress action
	Mt	total sample mass at time 't'
	M ₀	total sample mass at initial time (t = 0)
	M_∞	total sample mass at equilibrium (t = ∞)
	n	diffusional exponent
	Ν	number of polymer chains per unit volume
	R ²	coefficient of determination
	S	swelling function
	SS	shear stress function
	SD	soil dissolution function
	t	time
	Т	temperature

- Cartesian coordinates x, y, z
- Z frame at z-axis.

Greek symbols

- time step Δt
- Δz thickness step
- λ stretch in uniaxial direction (thickness at time 't'/dry state thickness)
- initial stretch initial swelling ratio (initial λο thickness/dry state thickness)
- stretch at equilibrium equilibrium swelling λ_{∞} ratio (equilibrium thickness/dry state thickness)
- Ω volume of a solvent molecule
- Flory-Huggins parameter. χ

Abbreviations

3-lactoglobulin
nigh-density lipoproteins
ow-density lipoproteins
nuclear magnetic resonance
partial differential equation
scanning fluid dynamic gauge
Whey protein isolate

Particularly, for protein-based soils, three stages can be identified in the cleaning process (Bird and Fryer, 1991):

- (1) Swelling: An initial swelling process occurs when the soil and the wash solution are put into contact. The diffusion of the liquid containing the active species causes the increase in thickness of the soil.
- (2) Erosion: Once the active species (e.g. enzymes) have had enough time to act and the increase in moisture content has weakened the soil structure, the removal of the substance starts to occur. A constant removal rate is reached for constant cleaning conditions. Swelling might still be occurring in parallel.

(3) Decay: In the final stages of the removal process, adhesive forces become important. For protein-based soils, adhesive forces are typically higher than cohesive forces (Liu et al., 2006). Therefore, higher energy input is required to remove the same soil amount. If cleaning conditions are invariant, then the removal rate is reduced in this latter stage until cleaning is complete.

Modelling cleaning processes over time is a complex task as different transport mechanisms are combined. Not many attempts have been considered so far and semi-empirical approaches are frequent. Dürr and Graßhoff (1999) developed a two-parameter exponential type model as an easy-to-use tool to predict cleaning. A specific time constant was defined as the time required to reach 63.2% of total removal. As a second parameter, a logarithmic-type slope characterising cleaning behaviour was also defined. The model showed high flexibility for describing different cleaning patterns. It was further expanded (Dürr, 2002) to re-appraise the model approach by using a Weibull distribution analysis.

Xin et al. (2004) proposed a mathematical model for the removal of milk protein deposits. Disengagement of protein molecules and subsequent mass transfer to the bulk of the wash solution (boundary layer) were considered to be the rate limiting stages. The initial swelling stage was constrained to occur before a 'reptation time' was reached and no cleaning was observed during this period. The 'reptation time' is linked to the initial time required for the first molecules to disengage. A first-order equation was proposed to characterise the removal rate and a disengagement rate constant introduced. This constant was considered as a function of the volume fraction of the disengaged protein molecules at the soil-solution interface. As the rate limiting stage is the movement of these molecules to the interface and their subsequent detachment, a critical concentration would be reached in this area and a constant removal rate obtained. This agreed with the results seen in experiments. Finally, the decay stage was modelled as a function of the surface area of the remaining film. By integrating the three steps, good correlations (no error given) were obtained with experimental data.

Extensive research has been done to study swelling and dissolution mechanisms on simple protein soil deposits such as β -lactoglobulin (β -lg). Studies performed (Mercadé-Prieto et al., 2007a) showed the presence of a dissolution threshold below which the gel swelled but did not dissolve. This threshold is a function of pH and the volume fraction available inside the protein network. It establishes the limit for the stability of the gels formed. An increase of pH increased the degree of swelling observed. Particularly, significant swelling occurred above pH 10. However, the addition of salts to increase of the ionic strength produced a screening effect between cations from solution and the polymer network. Thus, at a certain level the degree of swelling decreased. Dissolution occurred when pH was high enough (pH threshold) (Mercadé-Prieto et al., 2007b) and a certain swelling ratio was achieved (volume fraction threshold) (Mercadé-Prieto et al., 2009, 2007c). Dissolution rates varied for different alkalinities and solution ionic strengths. A sharp transition in the dissolution rate was found between pH 11 and 12. The disruption of non-covalent intermolecular bonds due to alkali denaturation was established as the main dissolution mechanism. This disengagement was favoured by the repulsion produced due to the increase in the number of charges and the subsequent unfolding of the

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