

# Clay and oxide destabilization induced by mixed alum/macromolecular flocculation aids

E. Pefferkorn

*Institut Charles Sadron (CNRS), 6 rue Boussingault, 67083 Strasbourg Cedex, France*

Available online 6 March 2006

This article is dedicated to Guy Chauveteau at the occasion of his retirement. G.C. always puts highest interest in this study. He initiated and always defended the project by the Institut Français du Pétrole that promoted the long term experimental investigations in the form of studentships and functioning grants.

## Abstract

The review points out typical differences and analogies of the bulk characteristics of aluminum ion complexed polyelectrolytes and of their adsorption behaviors when such systems were supplied to inorganic colloids such as oxides and clays. It reports some particular investigations that were carried out in aqueous media to determine (i) the nature of the interactions existing between clay or oxides, aluminum ions and polyelectrolytes and (ii) the effects on the interfacial characteristics and the colloid stability related to the relative concentrations of these different constituents. The investigations concerned the synthetic alumina/polyacrylic acid systems and the natural kaolinite/humic acid systems, as well as partly the mixed alumina/humic acid systems. Different adsorption features and destabilization kinetics were determined to develop within these systems. One of the main constraints of the investigation arose from the presence of three interacting components which developed amphoteric and amphipatic interactions, the latter being generated by the hydrophobic moieties induced by the aluminum ions/carboxylic acid groups ion-pairing. The investigations concerned the extent and the rate of transfer of hydrogen, aluminum ions and polyelectrolytes from the bulk solution to the solid surface. Electrical surface charge characteristics were expressed in terms of the  $\zeta$  potential of the colloid/polymer complexes. The colloid stability of the systems was determined as a function of time at short and long terms. The variation as a function of time of the number and weight average masses was correlated with the variation with time of the  $\zeta$  potential. All these systems were determined to reach the kinetic and thermodynamic equilibrium only slowly. Despite the fact that the supply of mixed coagulants provoked the initial aggregation and the subsequent fragmentation processes for both systems, the mechanisms responsible for the two processes were found to be different as revealed by comparatively investigating the synthetic and the natural systems. The fragmentation originated from the slow segregation process of positively and negatively charged groups for the natural kaolinite/humic acid systems, while the segregation process affected hydrophobic and hydrophilic moieties for the synthetic alumina/polyacrylic acid systems. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Polyelectrolyte; Polyampholyte; Polyacrylic acid; Humic acid; Alum/polyelectrolyte coagulation aids; Alumina flocculation; Kaolinite flocculation; Aggregation/fragmentation processes

## Contents

1. Introduction . . . . .	34
2. Physicochemical characteristics of the materials . . . . .	34
2.1. The aluminum oxide . . . . .	34
2.2. The kaolinite . . . . .	34
2.3. The polyacrylic acid. . . . .	35
2.4. The humic acid . . . . .	35
2.5. The aluminum ions . . . . .	35
3. Mutual interactions in polyelectrolyte solutions . . . . .	35
4. Mutual interactions in clay/ or oxide/polyelectrolyte dispersions . . . . .	37

*E-mail address:* [peffer@ics.u-strasbg.fr](mailto:peffer@ics.u-strasbg.fr).

4.1.	The polyacrylic or humic acid/aluminum oxide system . . . . .	37
4.2.	The humic acid/kaolinite system . . . . .	38
5.	Short term evolutions in oxide/ or clay/polyelectrolyte dispersions . . . . .	39
5.1.	The oxide/polyacrylic acid system . . . . .	39
5.2.	The oxide/humic acid system . . . . .	40
5.3.	The kaolinite/humic acid system . . . . .	40
5.4.	The amphoteric character of the kaolinite–aluminum ion–humate complex . . . . .	40
6.	Long term evolutions in the colloidal stability of oxide/ or clay/polyelectrolyte dispersions . . . . .	41
6.1.	The oxide/polyacrylic acid system . . . . .	41
6.2.	The kaolinite/humic acid system . . . . .	43
6.3.	Mechanisms of the aggregate breakup process . . . . .	43
7.	Conclusion . . . . .	44
	References . . . . .	44

## 1. Introduction

The adsorption of neutral polymer and polyelectrolyte on solid/liquid interfaces (clays, oxides, metals suspended in water) has been largely investigated because significant modifications of surface properties within the adsorbed layer are involved in the process. Especially, the presence of the interfacial layer on particles of colloidal size induced strong modifications of the suspension characteristics. Depending on the polymer/colloid relative concentration, colloid agglomeration or stabilization might be generated and are applied in water treatment [1–6]. This simple image cannot be extended to more complex environmental systems due to the diversity of the soluble and non soluble mineral and organic components of colloidal size. The retention or migration of micrometer-sized colloids in aquatic systems strongly depends on the concentration of soluble natural organic matter [7–13]. Thus, the interactions of natural polyelectrolytes with natural minerals and clays constitute a puzzling domain of investigation, insofar as the liquid phase generally contains ions of various types and electrical charges and the colloid itself may sustain different types of phenomena, e.g. dissolution or growth. Such interactions may develop in the aquatic environment, when the colloids are dispersed in a medium of constant electrochemical composition, the equilibrium conditions being imposed by the liquid phase. Such interactions may also develop in sediments and in relatively concentrated dispersions, when the electrochemical characteristics are imposed by the solid phase. In the latter case of intermediary colloid concentration, the modifications of the chemical characteristics of the supernatant may serve to determine the kinetics of the establishment of the thermodynamic equilibrium and its chemical characteristics.

In order to provide the most general information, the investigations focused on the mutual interactions existing between macromolecular systems, clays, oxides and soluble aluminum ions. Aluminum ions were present as dissolution products of the aluminum oxide at very small concentration in the synthetic [polyacrylic acid/aluminum oxide] and in the mixed [humic acid/aluminum oxide] systems under the given experimental conditions. Aluminum ions were supplied to the natural [humic acid/kaolinite clay] systems. Additionally, the colloidal stability of the different systems was investigated too. Finally, the role of the aluminum ions in the rate of aggregation/breakup of organic/

mineral agglomerates was presented and discussed. Knowledge of the mass distribution functions of aggregates and application of recent theories of reversible aggregation processes allow to determine the rate of aggregate breakup and to interpret the phenomena behind the fragmentation processes.

## 2. Physicochemical characteristics of the materials

### 2.1. The aluminum oxide

The  $\alpha$ -alumina of industrial origin (Aluminium-Péchiney) is partially soluble in water and its solubility depends on the pH of the dispersion. The dissolution of 0.4 g of the oxide in 50 ml of  $10^{-3}$  mol/l KCl aqueous solution at pH 5.0 produces aluminum ions whose concentration was determined to be  $10^{-4}$  mol/l after 2 h and constant for 24 h. These “equilibrium” conditions were instantaneously established by suspending the bare oxide in water containing  $10^{-3}$  mol/l KCl,  $10^{-4}$  mol/l  $\text{AlCl}_3$  at pH 4.06 [14]. The oxide developed a  $\zeta$  potential of  $58 \pm 1$  mV in the electrolyte suspension. The specific surface area determined by BET was  $3.0 \text{ m}^2/\text{g}$ . This sample is referred as Sample I.

The part of the sample employed to investigate the colloid stability was fractionated by six fold sedimentation. The recovered colloid particles were of diameter strictly larger than  $0.63 \mu\text{m}$ ,  $0.5 \mu\text{m}$  representing the lower detection limit of the TA II Coulter counter [15]. This fractionated sample is referred as Sample II.

### 2.2. The kaolinite

The clay was a kaolinite-type material of French origin (Kaolin des Charentes, code name GZA IV) [16]. The clay suspended in aqueous solution at pH 3.5 (0.5 g/l) was fractionated by sedimentation. Particles of very large size were allowed to settle out by gravity and were discarded, this operation being repeated five times. The morphology, composition and surface area characteristics are given in [17]. This sample I was used to investigate the aluminum ion/polyelectrolyte /kaolinite interactions. Kaolinite clay is not soluble in aqueous media at pH 5.0 but adsorbs aluminum ions from the liquid phase initially containing  $10^{-4}$  mol/l of  $\text{AlCl}_3$ . The Sample I was further fractionated in order to remove the upper portion of the suspended colloids. The corresponding clay was

Download English Version:

<https://daneshyari.com/en/article/591288>

Download Persian Version:

<https://daneshyari.com/article/591288>

[Daneshyari.com](https://daneshyari.com)