

CHEMISTRY OF WASTEWATER TECHNOLOGY

edited by

ALAN J. RUBIN

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PREFACE

This book deals with the physical chemistry of particle separations and other chemical aspects of wastewater processes. *Chemistry of Wastewater Technology* presents the latest research of interest to engineers and scientists as well as others concerned with environmental protection. Some of the topics covered in its 26 chapters include coagulation, precipitation, filtration, nutrient removal, adsorption and disinfection. The original papers were presented at a symposium sponsored by the Environmental Chemistry Division of the American Chemical Society. The highlight of the symposium was the keynote address of Dr. Werner Stumm on the occasion of his being presented the coveted ACS Pollution Control Award. His award paper, in this book as at the parent symposium, is introduced by Dr. James J. Morgan, a close associate of Dr. Stumm for many years. We, the co-authors of this book who have been so profoundly influenced by him, are pleased to acknowledge the many contributions of Werner Stumm.

The cooperation and efforts of the co-authors and the publisher's staff, particularly Jan Carter, in producing *Chemistry of Wastewater Technology* are greatly appreciated. The support of the Civil Engineering Department and the College of Engineering of The Ohio State University is also acknowledged.

Alan J. Rubin
Columbus, Ohio



Alan J. Rubin holds the bachelor's degree in civil engineering from the University of Miami and a master's degree in sanitary engineering as well as a PhD (environmental chemistry) from the University of North Carolina. The author of many publications and papers, Dr. Rubin is Professor of Civil Engineering and is associated with the Water Resources Center at The Ohio State University. He is also the editor of two other books published by Ann Arbor Science.

Introduction
to the
Award Address by the Recipient of the 1977
American Chemical Society Pollution Control Award
Werner Stumm

It is a pleasure both as a member of the American Chemical Society and as a colleague and friend of the author to provide a few introductory remarks for Professor Werner Stumm's Award Address, the keynote paper for this symposium on the *Chemistry of Wastewater Technology*. It is fitting that Professor Stumm be honored on the occasion of this symposium, in which chemistry figures so largely, for his career in aquatic chemistry has been dedicated to directing the attention of the profession to the effects of chemical parameters on water processes both in the natural environment and in technology. The Pollution Control Award, sponsored by Monsanto, recognizes Werner Stumm for his research contributions in the field of water pollution control. He has authored over 150 papers in his field. Examples of his innovative ideas and experimental results are to be found in such important areas as water and wastewater treatment, control of eutrophication, acid mine drainage, trace metals, and hydrocarbon pollution. In the wastewater treatment area Professor Stumm was one of the first to advocate and research the wider use of physical-chemical techniques to enhance the traditional modes of biological waste treatment. In this regard one can cite his work on flocculation of bacterial sludges and on the precipitation removal of phosphate nutrients. What has distinguished his work in all areas is that it has been new, it has been as quantitative as possible, and has been directed to areas of great practical concern in water quality management.

Werner Stumm is known as an inspirational teacher and colleague. He excites those with whom he works through the clarity of his ideas and the enormous energy and enthusiasm with which he approaches research problems. Without exception his students and collaborators have admired his didactic abilities and his research leadership. He communicates his enthusiasm to others. To quote from a recent editorial in *Environmental Science & Technology*, "It is also important to recognize Dr. Stumm's contribution to the

education of environmental scientists. These include his role in establishing aquatic chemistry as a subject with academic rigor and environmental utility, and also his inspirational teaching at Harvard and the Swiss Federal Institute of Technology."

Professor at the Swiss Federal Institute of Technology in Zürich, Switzerland, and Director of the Institute of Water Resources and Water Pollution Control, EAWAG, since 1970, Werner Stumm was, for the fifteen years prior, Professor of Applied Chemistry at Harvard University. He received his PhD in chemistry from the University of Zürich, where his major areas of interest were analytical and physical chemistry. He quite early saw the possibilities for applying ideas and methodologies for analytical and physical chemistry to problems in water chemistry, first as a research associate at EAWAG, then as a postdoctoral fellow in the Sanitary Engineering Department at Harvard in 1954-55. He joined the Harvard faculty in 1956. His research activities over his career have embraced studies in such areas as corrosion rates, kinetics of metal-ion oxidations, electrochemistry, coagulation and flocculation mechanisms, surface chemistry of metal oxides, nucleation processes, chemical oceanography, global chemical cycles, and chemical ecology of pollution. The impact of his work has been great.

Werner Stumm has been the PhD professor of more than a dozen students at Harvard and at EAWAG, and in addition he has worked with many more research fellows and visiting scientists and engineers in his laboratories. Since returning to Switzerland in 1970 he has established the chemistry department of EAWAG as a focal point for aquatic chemistry research and has attracted many, many visitors in the fields of chemistry, engineering, biology, geochemistry and oceanography.

This symposium comprises an impressive group of papers dealing with research and technical innovations in wastewater technology. The importance of chemical concepts in improving wastewater technology is evident from the subject matter represented in the symposium. It is an additional tribute to the keynote author that a dozen former students and research colleagues, or their students, are participants in the symposium.

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CHAPTER 1

CHEMICAL INTERACTIONS IN PARTICLE SEPARATION

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INTRODUCTION

The solid-solution interface is of particular importance in natural waters and in water treatment systems. Suspended particles in natural and waste-waters vary in diameter from 0.005 to about 100 μm (5×10^{-9} to 5×10^{-4} m). For particles smaller than 10 μm , terminal gravitational settling will be less than *ca.* 10^{-2} cm/sec. As suggested in Figure 1, filter pores of sand filters are typically larger than 500 μm . The smaller particles (colloids) can become separated either by settling, if they aggregate, or by filtration, if they attach to filter grains. Particle separation is of importance in the following processes: (1) aggregation of suspended particles (clays, hydrous oxides, phytoplankton, biological debris) in natural waters; (2) coagulation (and flocculation) in water supply and wastewater treatment; (3) bioflocculation (aggregation of bacteria and other suspended solids) in biological treatment processes; (4) sludge conditioning (dewatering, filtration); (5) filtration, groundwater infiltration; and (6) removal of precipitates (*e.g.*, phosphate elimination).

In the past few decades water supply and wastewater treatment have had to depend essentially on the same unit processes and unit operations; innovation and process improvement, especially improvement in process dynamics, had to come from a better engineering design rather than from new tools. Progress in engineering design of coagulation (followed by sedimentation, flotation or filtration) and filtration processes has been

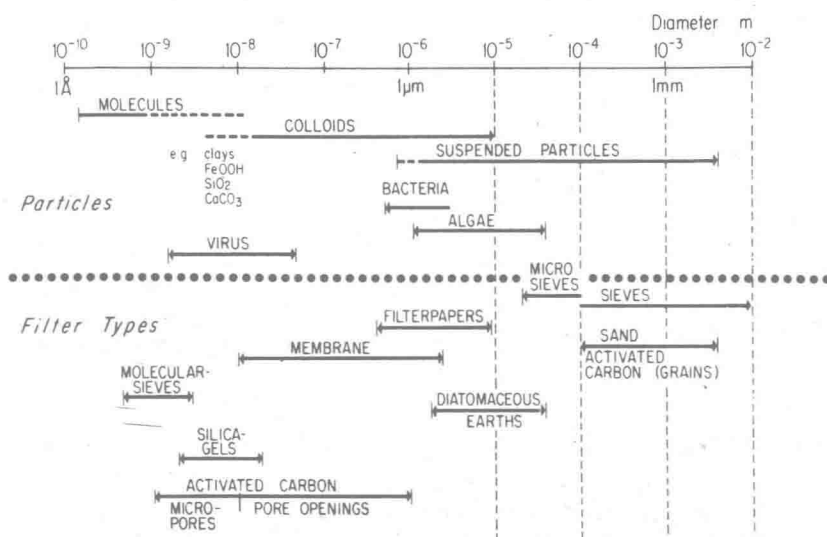


Figure 1. Size spectrum of waterborne particles and of filter pores.

achieved from a more thorough understanding of the process concepts. Considering separately the chemical (especially colloid and surface chemical) and the physical (including mass transport and fluid mechanic) aspects is of great help in assessing the variables and parameters that influence these processes. Coagulation and filtration may be rendered more dynamic or more efficient by modifying the chemical variables in such a way as to improve the efficiency of the collision between particles and particles and filter grains. Higher filtration rates may often be achieved without impairing the quality of the filtrate if a reduction in contact opportunities between suspended particles and filter grains (e.g., by a decrease of filter depth and medium diameter) is compensated for by a chemical improvement of the collision efficiency.

This chapter is organized as follows:

1. It shows how solution variables may influence the charge of colloidal surfaces. A simple case history will serve for illustration. The specific adsorption of cations (e.g., Mg^{2+} , Ca^{2+} , heavy metal cations and H^+) and of anions [e.g., SO_4^{2-} , HPO_4^{2-} , $\text{SiO}(\text{OH})_3^-$ and OH^-] on the surface of hydrous oxides of Si, Al^{3+} or Fe^{3+} affects the resultant net charge of these oxide particles.
2. It compares the effectiveness of particle aggregation in coagulation and particle removal in filtration, both in natural and in treatment processes,

and illustrates how they depend on contact opportunities, on the one hand, and on the efficiency of the contacts, on the other hand. The designer of a treatment process can choose among various chemical or physical variables.

3. It gives an application in practice. The removal of phosphate in complementary biological and chemical sewage treatment exemplifies some of the concepts discussed.

SPECIFIC CHEMICAL INTERACTION AND COLLOID STABILITY

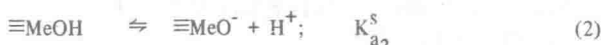
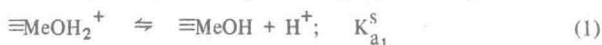
The presence of an electrical charge on the surface of particles is often essential for their existence as colloids; the electrical double layer on their surface hinders the attachment of colloidal particles to each other and to filter grains. The resultant net charge is sensitive to the composition of the aqueous phase because adsorption or binding of solutes to the surface of the colloids may increase, decrease, or reverse the effective charge on the solid. Adsorption occurs as a result of a variety of binding mechanisms: electrostatic attraction or repulsion, covalent bonding, hydrogen-bond formation, van der Waal's interaction or hydrophobic interaction. One speaks of specific chemical interaction if binding mechanisms other than electrostatic interaction are significantly involved in the adsorption process.

Chemical destabilization of colloids is achieved in coagulation (or flocculation) and contact filtration by adding substances which enhance the aggregation or attachment tendency of these colloids. Natural and synthetic macromolecules (often polyelectrolytes) have a strong tendency to accumulate at interfaces and have been used successfully as aggregating agents. The Fe^{3+} and Al^{3+} salts used as coagulants and destabilizers belong also to this category because they form polynuclear hydrolysis products, $\text{Me}_q(\text{OH})_n^{z+}$, which are adsorbed readily at particle-water interfaces. That specific chemical interactions contribute significantly to the adsorption and colloid destabilization is evident from the observation that these coagulants, at proper dosage, can reverse the charge of the colloid. Colloids also become less stable with increasing concentrations of indifferent (not specifically interacting) electrolytes because the diffuse part of the electrical double layer becomes compressed by counter-ions¹⁻⁴

Interactions of Cations and Anions with Hydrous Oxides

Oxides, especially those of Si, Al and Fe, are abundant components of the earth's crust; they participate in many chemical processes in

natural waters and often occur as colloids in water and waste treatment systems. The colloid stability of hydrous oxides may be affected by electrolytes in a different way than that of hydrophobic colloids. Specific adsorption of cations and anions on hydrous oxide surfaces may be interpreted as surface coordination reactions.^{3,5-8} As indicated in Figure 2, hydrous metal oxides exhibit amphoteric behavior and can, at least operationally, be compared with amphoteric polyelectrolytes.



Since H^+ and OH^- ions are primarily the potential determining ions for hydrous oxides, alkalimetric or acidimetric titration curves provide a quantitative explanation for the manner in which the charge depends on the pH of the medium,⁶⁻⁸ as indicated in Figure 3.

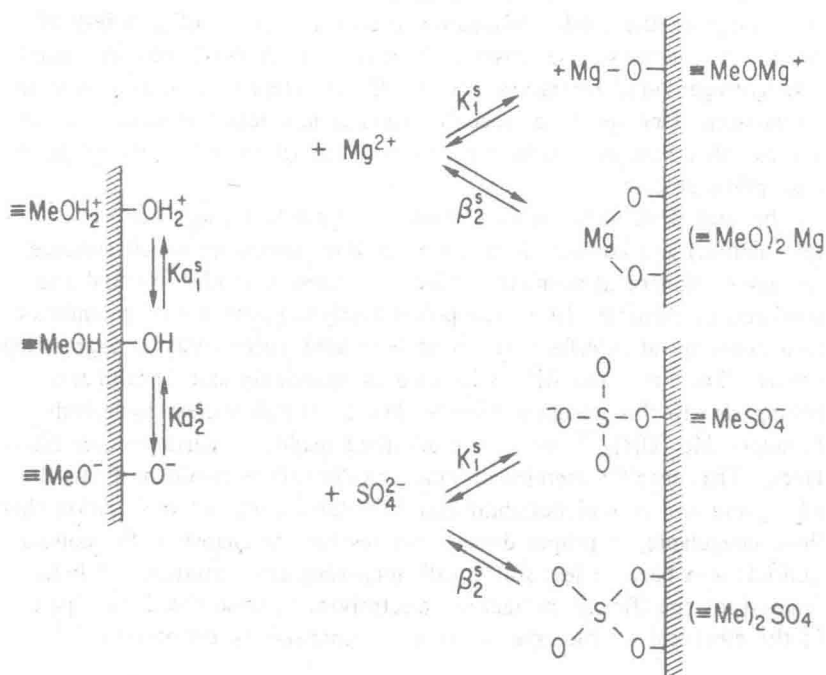


Figure 2. Interactions of hydrous oxides with cations and anions can be interpreted in terms of surface complex formation and ligand exchange equilibria.

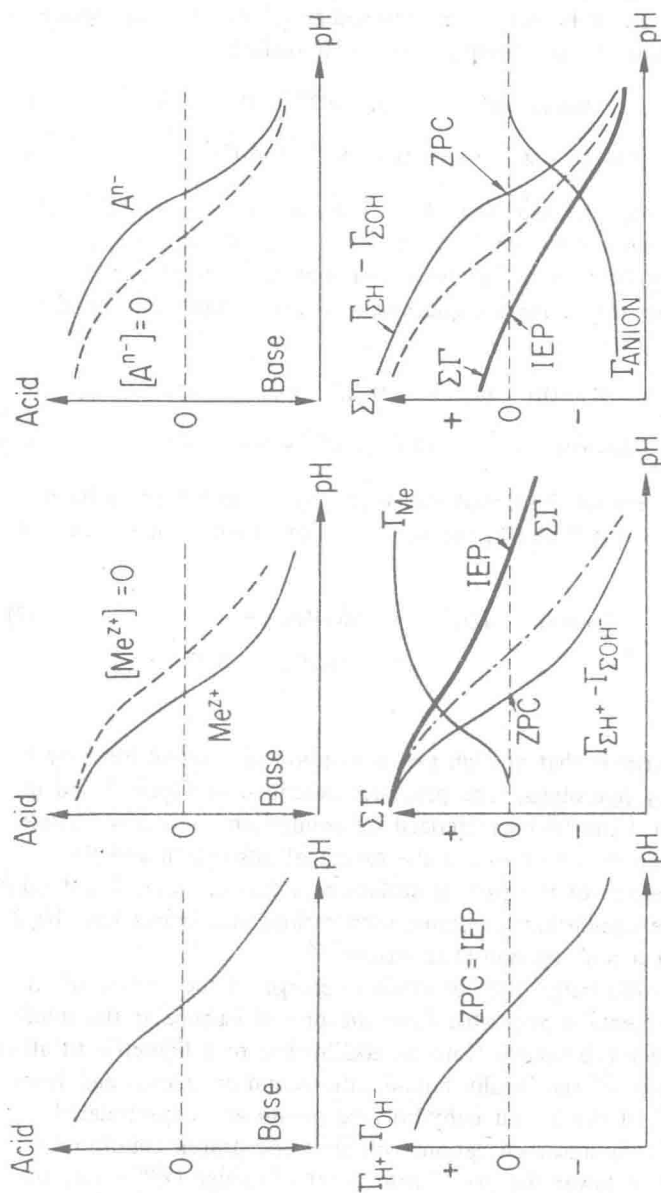
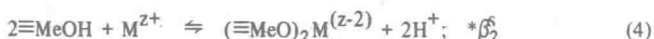
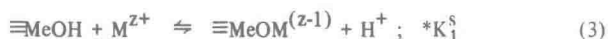
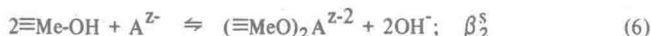
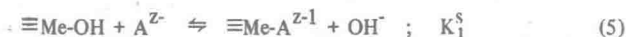


Figure 3. The net charge at the hydrous oxide surface is established by the proton balance (adsorption of H^+ or OH^- and their complexes) at the interface and specifically bound cations or anions. This charge can be determined from an alkalimetric-acidimetric titration curve and from a measurement of the extent of adsorption of specifically adsorbed ions. Specifically adsorbed cations (anions) increase (decrease) the pH of the isoelectric point (IEP) but lower (raise) the pH of the zero point of charge (ZPC).^{6,8}

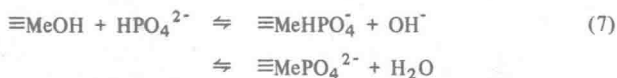
Operationally, there is a similarity between H^+ , metal ions and other Lewis acids. The OH groups on a hydrous oxide surface have a complex-forming O-donor group like OH^- or OH groups attached to other elements (phosphate, silicate, polysilicate). Proton and metal ions compete with each other for the available coordinating sites on the surface:



The extent of coordination is related to the exchange of H^+ by M^{Z+} ions; *i.e.*, it can be measured by the displacement of an alkalimetric titration curve. Similarly, ligand exchange with coordinating anions leads to a release of OH^- from the surface and a displacement of the titration curve in the other direction



For protonated anions the ligand exchange may be accompanied by a deprotonation of the ligand at the surface. For example, in the case of HPO_4^{2-}



it is also conceivable that at high pH, adsorption of a metal ion may be accompanied by hydrolysis. The processes described in Figure 2 and in Equations 1 to 7 can be characterized by equilibrium constants. These constants can be used to estimate the extent of adsorption and the resultant net charge of the particle surface as a function of pH and solute activity. Some equilibrium constants with cations and anions have been determined for a few representative oxides.⁶⁻⁸

As Figure 3 illustrates, the net resultant charge at the surface of an oxide is experimentally accessible from the proton balance at the solid-solution interface (obtainable from an alkalimetric or acidimetric titration curve in presence of specifically bound cations and/or anions) and from a measurement of the bound unhydrolyzed cation and deprotonated anion. Specifically adsorbed cations will shift the proton condition in such a way as to lower the pH of zero point of charge (ZPC); *i.e.*, the pH at which that portion of the charge which is due to H^+ or OH^- ions or their complexes becomes zero. Because of the binding of M^{Z+} , the

resultant net charge increases, or becomes less negative, and the pH at which the resultant net charge becomes zero, the isoelectric point (IEP), is shifted to higher pH values. Correspondingly, specifically adsorbing anions increase the pH of the ZPC but lower the pH of the IEP.

Figure 4 illustrates that cations and anions typically present in a natural water become specifically adsorbed at an aluminum oxide surface and modify its charge. The adsorption of SO_4^{2-} causes a reduction,

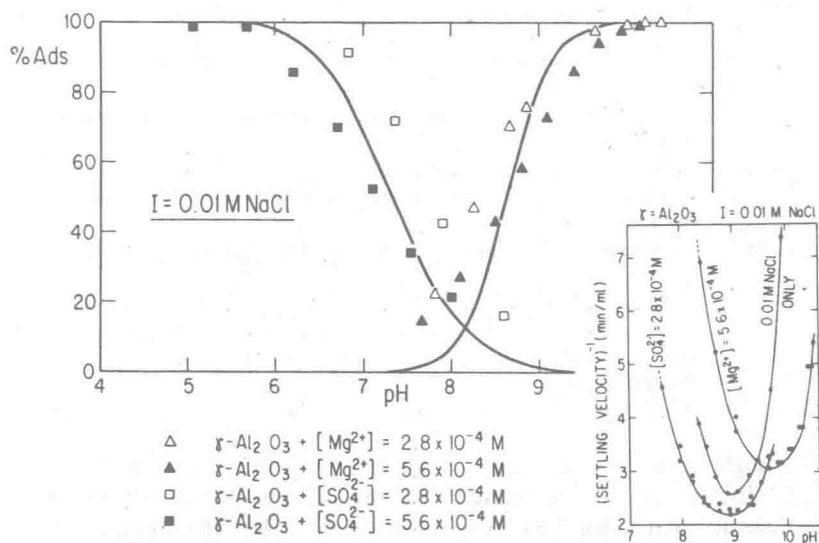


Figure 4. Extent of specific adsorption of SO_4^{2-} and Mg^{2+} on Al_2O_3 . The drawn out lines have been calculated from experimentally determined equilibrium constants for the adsorption from a $5.6 \times 10^{-4} \text{ M}$ MgSO_4 solution. As shown by the insert, Mg^{2+} causes an increase and SO_4^{2-} a decrease in the isoelectric point (maximum settling rate).

while the adsorption of Mg^{2+} causes an increase in charge (compare Figure 2). The concomitant shift in the pH of the isoelectric point becomes apparent in sedimentation experiments because maximum settling velocities of suspended particles are observed at zero charge.

PARTICLE ATTACHMENT IN COAGULATION AND FILTRATION

The kinetics of particle transport and particle attachment determine to a large extent the various particle removal processes in natural waters