Chapter 1
Introduction

1.1 Background

Urban wet-weather flow (WWF), which includes sanitary sewer overflow (SSO), combined sewer overflow (CSO), and stormwater discharge (SWD), contains significant quantities of toxic substances. WWF related toxic pollutants are major contributors to the degradation of receiving waters. Urban WWF contains a greater variety of toxic pollutants than sanitary wastewater. Pollutants carried off urban catchments by drainage systems during wet weather originate from many sources, e.g., commercial, industrial, and residential parking areas; roadways; automobile-service stations; sewer infiltration from leaking underground storage tanks; accidents and spills; park and residential lawns; construction sites; and active and inactive industrial sites. Past studies indicate that SSO, CSO, and urban SWD contain significant quantities of toxic substances; a number of the hazardous-waste priority pollutants have been identified. Without consideration of urban and industrial stormwater-runoff toxic-substance control, the various hazardous-substances-cleanup programs will not be effective in controlling total area wide emissions of these substances.

Toxic-organic chemicals (e.g., benzene, polynuclear aromatic hydrocarbons [PAH], polychlorinated biphenyls [PCB], etc.) and heavy metals (arsenic [As], cadmium [Cd], chromium [Cr], copper [Cu], lead [Pb], mercury [Hg], and zinc [Zn]) in storm-induced discharges contribute to receiving-water degradation (Pitt, et al., 1995). The US Geological Survey reported that urban storm runoff collected from residential, commercial, and industrial areas around Phoenix, AZ was found to be toxic to fathead minnows and water fleas (Lopes and Fossum, 1995). Industrial and commercial parking lots, material storage areas, and vehicular service stations are the most significant contributors of such pollutants to WWF as reported by Pitt, *et al*.(1995).

Sansalone *et al*. (1995) observed that lead, predominantly associated with the particle fraction, was more mobile than copper for highway runoff. Water quality in a creek below a highway construction site indicated that the sediment concentrations of total hydrocarbons, aromatic hydrocarbons, and heavy metals and water concentrations of heavy metals and selected anions increased downstream of roadway runoff (Maltby *et al*. 1995). Hydrocarbon contamination of sediments was positively correlated with potential contaminant loading functions (that is, length of road drained/stream size). Boudries, *et al.* (1996) and Estèbe, *et al*. (1996) reported that heavy metals and aliphatic and aromatic hydrocarbons bound to particles in the River Seine sediments near Paris are due to urban WWF discharges. Such toxic substances in sediments create a long-term impact on ecological systems.

Most of the solids finer than 50 micrometers(μm)are the principal vector of pollution in urban stormwater (Chebbo *et al., 1990*). Table 1-1 that summarizes results from urban storm runoff characterizations by Ellis and Revitt (1982) and Vignoles and Herremans (1995) indicates the majority of heavy metals are associated with particles less than 10 μm which are well into the colloidal range. Thus, in order to effectively control toxic heavy metals in urban stormwater, treatment processes that are capable to remove fine particles (<10 μm)and to be able to handle unsteady-nonuniform stormwater flow must be used. However, very few of the commonly applied physical-chemical processes are cable to remove such fine particles effectively.

Table 1-1. Metal Distribution Versus Particle Size

Suspended solids Size (micrometers)	Metal Distribution (%)							
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
> 100	18	9	5	7	8	8	4	5
10 -- 100	36	31	24	30	21	29	23	35
< 10	46	60	71	63	71	63	73	60

One approach of removing small particles in urban WWF is to apply coagulant to promote colloid sorption during floc formation prior to sedimentation than followed by filtration. These processes achieve better solids removal than the plain sedimentation (retention tank); but unsteady stormwater flow can detrimentally affect the process efficiency. In recent years, micro-sand has been used as weighted microcarrier (MC) in ballast-coagulation of colloidal particles accelerating settling velocity. This is a new high-rate physical-chemical clarification process. It was originally designed for drinking water treatment and recently being tested for treating wastewater and WWF. This process consists of the addition of a coagulant in the influent pipe, MC and coagulant aid (i.e., flocculant, polymer, polyelectrolyte) in a mixing chamber, and than followed by maturation (flocculation) and sedimentation tanks. The initiation of the reaction of coagulation-flocculation processes is improved by the presence of the MC and polymer, which increases the bonding of the floc to the MC, resulting in higher settling velocities. The Microsep® (U.S. Filter Corporation) and the Actiflo® (Omnium de Traitement et de Valorisation [OTV]) are two commercially available systems that use recycled MC (e.g., microsand), while DensaDeg® (Infilco Degremont, Inc.) recycles its sludge. Recently, these processes are being evaluated at an increasing number of pilot units for treating CSO.

1.2 Purpose of Study

In view of the difference between MC and conventional coagulation-flocculation processes, the existing bench-scale testing procedures or standard Jar Test may not be adequate. Thus, there is a need for developing a new set of bench-scale testing procedures. The main purpose of this study is to develop and evaluate new MC bench-scale (Jar Test) procedures for engineers or plant operators to screen and select the effective combination of type-dosage of coagulant, MC, and coagulant aid for removing WWF colloidal particles. Determination of the particle size distribution and zeta-potential of colloids enable a better selection of coagulation-flocculation agents for the MC weighted coagulation process. Results of the experimental study herein may offer useful information to provide a framework for further evaluation on MC weighted coagulation for subsequent researchers.

Objectives

The objectives of this investigation are to:

- Evaluate the applicability of conventional jar test procedure to the MC weighted coagulation, and if needed, modify the jar test procedure for screening MCs, coagulants, and coagulant aids;
- Test the effects of different types and dosages of coagulant and coagulant aid in conjunction with MC for selection of the most effective combination;
- Investigate the effect of MC on particle size distributions and zeta potential of colloids in urban WWF by using the modified jar test procedure.

Presented below is a brief review related to the phenomenon of coagulation.

1.3 Colloids Coagulation Analysis

Colloid coagulation is a complex process which depends on a number of factors such as colloid type, particle concentration, pH, coagulant concentration, particle size distribution, surface area, surface charge, interfacial reactions and collisions between suspended particles (Gregory, 1993). Mathematically, the coagulation process is known to be a binary process that has been modeled as a second-order rate process (for example, O'Melia, 1993): $dn/dt = kn^2$, where n is the concentration of particles in suspension at time t, and k is a second order rate constant. From a mechanistic point of view, coagulation depends on two distinct influences: (a) particles must move in such a way that collision occurs; and (b) interaction between colliding particles must be such that permanent contacts can be formed. These two factors are related to the rate constant mathematically as $k = \alpha\beta$, where α is a dimensionless sticking coefficient associated with the colloidal stability while β is a mass transport coefficient depending on the transport mechanics and their particle interactions. Various approaches have been proposed for determining these coefficients. In general, β is evaluated from a micro-hydrodynamics standpoint and α is determined indirectly from experimental results. It should be pointed out that although micro-mechanisms of colloidal particle coagulation have been studied extensively for chemical and biological applications, interest in water and wastewater treatment applications only began in the late 1960's. In any case, the interest in environmental studies was provided by the advances in environmental engineering, especially in the theory of interparticle forces, coupled with the development of new experimental techniques.

Mass Transport Coefficient (β)

Suspended particle collisions occur in water due to velocity variations caused by three different processes, namely, Brownian diffusion, fluid shear, and differential settling. Generally, particles less than 0.1 micrometer in diameter may be dominated by Brownian diffusion while particles larger than about 5 micrometers may be transported by settling. Particles in the range of 0.1 to 5 micrometers are too large for Brownian diffusion and too small for settling.

By assuming that all particles move in straight lines until contacts occur between them, a rectilinear model was established by Smoluchowski. The expressions of β for each of the three different transport mechanisms have been determined analytically (e.g., Clark, 1996). This model is considered to be the most fundamental approach in colloidal coagulation analysis. However, the rectilinear model neglects the hydrodynamic influence and the short-range interactions between approaching particles. Moreover, as aggregates grow in size, transport mechanisms change, aggregate morphology is altered, and breaking up by hydrodynamic forces can occur. Recently, questions were raised with regard to the validity of the rectilinear modeling approach. Han and Lawler (1991) modified this model using a curvilinear track for particle motions by adding hydrodynamic considerations.

However, interparticle reactions have not been included in the analysis.

Colloidal Stability (α)

Given the possible collisions between particles, stable particles have to be transformed into unstable ones in order to complete the coagulation process. Experiments to determine the colloidal stability in aquatic systems are scarce. Theories about the origins of colloidal stability in aquatic systems are few and qualitative and none has been tested experimentally. The present status is described well by Professor O'Melia: "Theories of colloidal stability are helpful in understanding why particles are stable and in identifying important chemical properties of solutions and solids that affect stability, but they are not able to provide accurate quantitative predictions of coagulation rates when chemical repulsive interactions produce low attachment probabilities (low alphas)." (O'Melia, 1993).

Particle Interactions

The earliest and still the only quantitative analysis of colloid stability is the DLVO theory, developed independently by Derjaguin and Landau (1941) and Verwey and Overbeek (1948). Essentially, they combine the Van Der Waals attraction (caused by dipole moments in the constituent molecules of two approaching colloidal particles) and the electrical double layer repulsion to give the total energy of interaction between particles as a function of the separation distance. All other types of interactions are ignored. In addition, the theory is dependent on factors such as colloid type, particle concentration, pH and coagulant concentration.

Analytical formulation of the double layer was developed independently by Gouy and Chapman who derived the fundamental equation relating electrical potential to charge in the diffuse layer (Russel, et al, 1989). The potential at the plane of shear within the double layer is known as the Zeta potential. It depends on the thickness of the double layer and its value determines the extent of the electrostatic forces of repulsion between charged particles. The seta potential is a useful and important tool in providing information on the optimum coagulant dosage for the microcarrier process.

Fractal Approach

The problem of characterizing particle size becomes somewhat complicated for natural particles and their random aggregates. Fractal theory has been explored to study this process (e.g., Lin, et al., 1989; Meakin, 1988). Since random aggregates contain greater surface area than any equivalent sphere or other shape, the aggregate is more of a 'tenuous' surface (two-dimensional) rather than a three-dimensional object. For a large number of aggregates, if the mass is plotted against aggregate size on a log-log scale, the plot may be linear with a non-integer slope. The relationship between aggregate mass *(M)* and size *(L)* can be expressed as $M = L^d$, where the 'slope' *(d)* of the line is called the fractal dimension. For a regular two or three-dimensional object, the slope is either two or three, respectively. The lower the fractal dimension, the more open the aggregate structure. As the coagulation of solid particle proceeds, fluid is incorporated into pores in the aggregates that are formed. Aggregate density decreases and total aggregate volume increases as the process continues. The result is that the target cross sections or collision diameters of the aggregates increase thereby increasing the rates of interparticle contact brought about by Brownian diffusion, fluid shear and differential sedimentation. Observations of natural and technological systems indicate that the aggregates in these systems are fractals and have fractal dimensions less than three.

Relevant Aspects

In the past, considerable attention has been given to describing airborne-particle capture in flow past simple collector geometries, especially cylinders (Pruppacher and Klett, 1978; Wen, 1996). There are similarities between the capture of gas-borne particles and liquid-borne particles based on computed forces from fluid mechanics theory. However, important dissimilarities exist for kinds and magnitudes of other forces not based upon the field of fluid mechanics such as electrostatic force. Other factors such as different molecular mean free paths for gases and liquids also play an important role in the coagulation process.

1.4 Organization of Report

This report consists of six chapters and two appendixes with associated references. First, Chapter 1 presents a background review on the MC process followed by statement of the primary objectives of the study and a brief review of colloid coagulation phenomena of colloids related to water treatment. Chapter 2 describes the major apparatus, instruments and testing procedures used in this study. The experimental program is presented in Chapter 3, which includes sample preparation and three stages of experimental design, namely, prescreening, screening, and confirmative tests. Chapters 4 and 5 present experimental results for surface runoff and CSO jar-tests, respectively. Summary and recommendations are discussed in Chapter 6. Appendix A presents a quality assurance statement. Appendix B describes the zeta potential measurement procedures recommended by the manufacturer. In addition, experimental results are presented in Appendix C.