Introduction to the Theory of the Streaming Current Meter

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Introduction

A streaming current (SC) meter is an instrument for measuring the charge that exists on small, suspended particles in liquid. A streaming current meter (SCM) is the only online instrument that can be used to measure coagulated particle stability for the feedback control of coagulant dosage.

The streaming current meter (SCM) is also referred to as the streaming current detector (SCD) or streaming potential detector (SPD) as well as streaming current monitor and streaming current analyser (SCA) in various works. The word 'detector' is used in earlier literature instead of the words 'meter', 'monitor' or 'analyser' because earlier SCMs were considered to only provide a qualitative indication of the presence and sign of charge, rather than a useful quantitative measurement. The words 1: 'Meter', 2: 'Monitor' and 3: 'Analyser' all mean the same thing in this context, except that the implication of sophistication increases in this order.

The difference between streaming potential and the more useful streaming current will be explained in the following section.

This paper uses the more modern and descriptive term streaming current meter for all of these instruments.

Colloidal Particles

Turbidity is caused by suspended particles in water in the size range of approximately 0.01 to 100 um in size. The larger fraction can easily be removed by settling. The smaller particles, with sizes of less than 5 um are referred to as colloidal particles (or colloids) and have extremely slow settling velocities and so cannot be practically removed by settling. The behaviour of colloidal particles in water is strongly influenced by their electrostatic charge. This colloidal charge comes about because of the uneven surface characteristics of the particles and in most solids is negative, particularly the alumino-silicate clays typically suspended in surface water. The charge on each particle will repel others and prevent significant flocculation from occurring. Neutralising this charge is the main purpose of coagulation.

However, simply considering the charge as an electrostatic surface charge is an over simplification. As the whole solution must have a neutral charge, a layer of water containing ions of opposite charge surrounds each colloid. Consideration of colloidal charge purely in terms of the colloidal particles by themselves has no benefit, as the surrounding ions are, for all practical purposes, inseparable from them.

The Double Layer

The double layer model is used to explain the distribution of ions around each colloidal particle. This is a long standing conventional approach to colloid analysis, a more detailed description is available in a number of works on this subject (eg Bratby 1980).

For illustrative purposes we will assume a negatively charge colloid. Closest to the negative surface of the colloid there is a layer of strongly bound positive ions – this is know as the Stern layer. Further positive ions are still attracted to the colloid but are repelled by the Stern layer; likewise, negative ions are attracted to the positive ions but repelled by the colloid. A dynamic equilibrium of negative and positive ions forms outside the Stern layer, known as the diffuse layer. The concentration of positive ions in the diffuse layer gradually decreases as the distance from the colloid increases until beyond a certain distance the ion concentrations are the same as the equilibrium in the water.

The strongly held positive ions near the surface and the charged layer surrounding this is where the name double layer comes from. The point just outside the stern layer is often called the shear plane as motion of the particle through the water shears the diffuse layer away.

The thickness of these layers depends on the concentration of ions in solution. At any distance from the surface the charge density is equal to the difference between the concentration of positive and negative ions at that distance. This results in an electrical potential (which is a voltage, caused by separation of charges) existing across the layers. This potential is greatest near the surface and decreases to zero as the distance from the colloid increases. A graph of this potential curve is useful because it indicates the distance at which the interaction between colloids will occur.

This is illustrated in Figure 1.

The potential at the boundary between the Stern layer and diffuse layer is called the zeta potential. Zeta-potential is useful, as it is a direct indication of the amount of energy required to bring separate particles together.
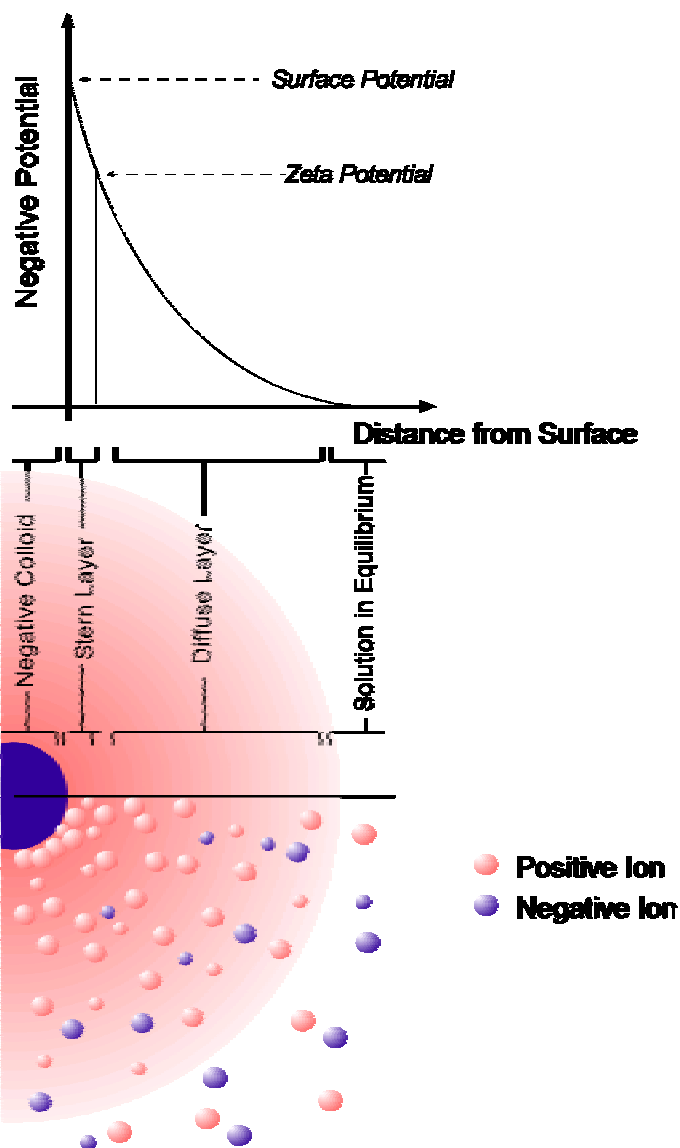
Figure 1 Ways to visualise the Double Layer model and the potential as a function of distance from the colloid's charged surface.

In fresh water suitable for treatment, the diffuse layer is large compared to the stern layer and so zeta potential gives a good indication of surface potential, which is directly related to surface charge. Zeta potential can be measured quite easily. This is done by using a microscope to observe turbidity particles inside a thin chamber called an electrophoresis cell. An electric field is applied along the cell, if the particles are negatively charged they will move towards the positive end of the cell, carrying their stern layer ions with them. The average speed with which these particles move depends on the zeta-potential, as it is this that determines the net electrical force operating on the particle and its stern layer ions.

In practice, the relationship between zeta-potential and this average speed is not always straightforward to calculate, as it is dependant on the fluid's viscosity, dielectric constant, conductivity and temperature. As a result, zeta potential, which should have units of mV, is often expressed in terms of electrophoretic mobility. This

has rather confusing units in velocity per electric field strength, typically um/s per V/cm.

Other disadvantages of measuring zeta-potential in this way include:

- It can only be determined for particles that are large enough to be detected and tracked through a microscope.

- It requires a lab technician to operate the apparatus and to observe the particles through a microscope. Therefore, Zeta potential measurement is slow, labour intensive and cannot be used online.

- It is not very accurate near zero, which unfortunately is the point of greatest interest, because of the difficulty in tracking the particle motion.

Zeta-potential measurement has applications in laboratory studies of coagulation and flocculation processes, but is of little use for online automation.

The Streaming Current Effect

The streaming current (or streaming potential) effect is a reverse manifestation of the electrophoresis effect. This occurs when a particle is mechanically moved through the fluid, or the fluid moved past the particle, resulting in a separation of charges causing a potential to exist.

A commonly situation occurring situation is that water with negatively charged particles is forced through a filter. The negatively charged particles become lodged in the filter, while the mobile positively charged ions are swept downstream. This separation of charges causes an electrical potential to exist across the filter, called the streaming potential. If electrodes are inserted upstream and downstream of the filter then the electrical potential can be measured. The upstream electrode is negative and the downstream electrode is positive. (Electrical potential is also referred to as voltage, as it is measured in unit called Volts.)

The electrical potential results in a current being conducted upstream through the water to remove the charge separation, this is the streaming current. The electrical potential therefore depends on the conductivity of the liquid. If the electrodes are connected together by a path with a much higher conductivity than the water, such as a wire, then the current will flow mostly through this path and little potential will exist.

Streaming current is a more fundamental quantity than streaming potential, as it does not depend on the water's conductivity.

Streaming current can be measured whenever the water with suspended charged particles is forced through thin capillaries or other barriers to the particle's motion. However, useful measurements are extremely difficult to directly make from this effect, as the current produced is extremely small and easily obscured by potentials that exist for other reasons and electrical paths through the environment. Difficulties such as the dc offset in the electronics and electrode drift make this simple approach virtually impossible to use in a practical sensor.

Strictly speaking, zeta-potential is a property of a surface, rather than of a group of particles. A variety of surfaces can produce zeta-potential (and streaming current) in water. These, normally insignificant, effects are well recognised in materials science. This work, however, uses those terms in the manner typical of discussion focused on water treatment, and considers them to be bulk properties of suspended colloids. Thus a sample of turbid water is said to have a certain streaming current, when correctly it is the average zeta-potential of the surfaces of the suspended colloidal particles that produces a certain streaming current in a certain sensor[1].

A Practical SCM Sensor Design

The practical streaming current meter (SCM) was invented around 1966 and credited to F.W Gerdes. Gerdes' approach overcomes many of the limitations of direct streaming current measurement (Gerdes 1966 a and b) and is the basis for all modern SCMs.

The SCM is based on the effect where the walls of the capillaries through which the colloidal material flows quickly gain a coating of particles and take on the surface charge characteristics of these particles. The SC sensor consists of a piston and a close-ended chamber. A narrow gap, an annulus 200-500um wide, exists between the piston and the walls of the chamber The piston is driven up and down at a fixed frequency, typically 4-5 strokes per second, forcing sample water in and out of the chamber through the annulus. A typical SC sensor is shown in Figure 2.
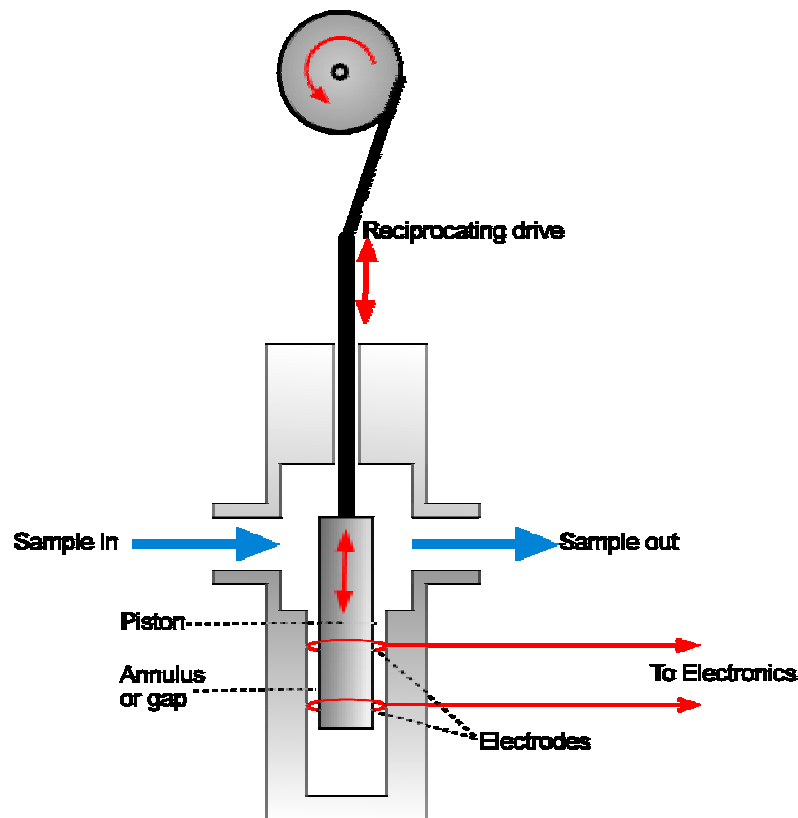
Figure 2 Streaming current sensor.

As the piston and chamber surfaces are coated with charged particles, the water flowing rapidly up and down through the annulus results in displacement of the counter-ions. The SC signal measured by electrodes in the annulus is proportional to the water velocity and therefore alternates in time with the piston. This signal is typically in the range of 0.05uA to 5uA depending on the particular conditions.

Measurement of SC in a closed chamber has several advantages compared to measurement directly in a flowing stream:

- The closed end is electrically isolated and removes problems caused by large potentials in the process stream from other sources.

- The signal is alternating at the frequency of the piston. This allows it to be separated from external noise and offset caused by electrode drift and dissymmetry.

- Practical aspects of instrumentation, such as that the closed chamber can be shielded from electromagnetic interference and cleaned easily.

Theoretical Description

Unfortunately, a complete, quantitative and verified mathematical description of the sensor does not exist.

Several attempts have been made at modelling the SC sensor. The original approach by Gerdes (1966a) was based on a simplified triangular fluid velocity profile within the annulus. Later work (Elicker et al 1992) used a more appropriate fluid profile model. The most complete work to date also considered inertial effects within the annulus and compared the solutions with those found by earlier methods (Walker et al. 1996). They found that for the geometries used by typical SCMs, the earlier approximate solutions produce very similar results to their more complete model.

All of these models have the following form:

$$I = k.s.\omega.\varepsilon.\zeta.f(r,R)$$

Where I=average current magnitude, s=piston stroke length, ω=motor cycles per second, ε=dielectric constant of solution, ζ=zeta potential, r= piston radius, R=chamber radius, k=electronics gain constant, f()=a function of the annulus shape which depends on the model used.

Experimental results show that the linear relationships with s and ω exist as predicted (and, of course, k). Likewise, results have shown that I is generally linearly related to ζ. However the model's predictions of the actual I measured are generally poor.

All the models assume that the surface of the piston is completely and uniformly coated by the colloidal particles and by any coagulant in solution in a representative manner. This is not necessarily a valid assumption and probably goes a long way towards explaining the poor predictive abilities of this theory (Barron et al. 1994; Dentel and Kingery 1989; Dentel et al. 1989a). Gerdes acknowledged the poor predictive abilities of this type of model, and acknowledged the existence of double-

equilibrium theory. This states that the charge on a particle surface is the result of an equilibrium between the ions on the surface and in the solution. The charge on the piston surface depends on another but similar equilibrium between the same concentrations in the liquid and a different adsorbed density on the piston surface. The charge on the two different types of surfaces, which are both in equilibrium with the same liquid, will be related to one another in a way that depends on their respective equilibrium constants. Using this theory, it is only possible to predict that any change in the colloidal system that changes zeta-potential will change SC in the same direction.

The modern colloidal-science theory works implicitly reject this equilibrium-based theory and provide no discussion of how, or at what rate, the measurement surfaces take on the zeta-potential characteristics of the sample. If an equilibrium does exist between the charge on the particles in solution and the charge on the measurement surfaces then it would influence the rate at which measured SC responds to changes in coagulant dosage. Indeed it can be shown that by starting with this assumption it is possible to develop a simple dynamic model that is a good fit for the sensor's observed dynamic response (Edney 2005).

Even if a perfect theoretical model of the SC sensor was possible and did exist, it would still be of limited practical use. This is because it would require complete characterisation of the piston surface and the precise geometry of the annulus. Surface characteristics and the tight tolerances are easily altered by physical wear and tear, even over relatively short time frames. It is quite possible to calibrate an SCM so that it reads directly in units of zeta-potential over a limited range or in units matching another SCM (Elicker et al 1992; Dentel et al 1989a), however it will not stay calibrated like this when in continuous use as the condition of the surfaces changes with time.

The unit of SC should properly be the unit of current (the Ampere). However, the lack of a consistent relationship between this and any useful physical or chemical parameters means that SCMs normally use arbitrary units. Their scales are designed to be adjusted for convenience and can be arbitrarily set by their users. This thesis will follow this convention and use the term 'SC units' to refer to arbitrary units used to measure SC.

Usage and History

The most useful way to apply a SCM in a typical water treatment plant is for the feedback control of coagulant dosage. The sample is taken from after the rapid mixing stage and the SC continuously measured so that a controller can adjust the coagulant dosing rate to maintain a set SC. This is illustrated in Figure 3. The SC that corresponds to the desired plant operation is traditionally determined by manual jar tests.

Figure 4 shows a typical relationship between alum dosage, SC of the dosed water and residual turbidity from the clarifier or jar tests. The SC that corresponds to minimum residual turbidity is typically offset slightly from zero, because of effects other than charge neutralisation. Generally a residual turbidity that is slightly less than the minimum is considered acceptable in order to reduce coagulant usage.

As the raw water turbidity changes, the coagulant to residual turbidity graph shifts considerably, while the relationship between SC and residual turbidity stays much more constant. Controlling the coagulant dose such that the SC is constant at the desired set point will result in a much more consistent residual turbidity. Often coagulant chemical savings can be achieved because conservative over dosing under manual control is avoided.
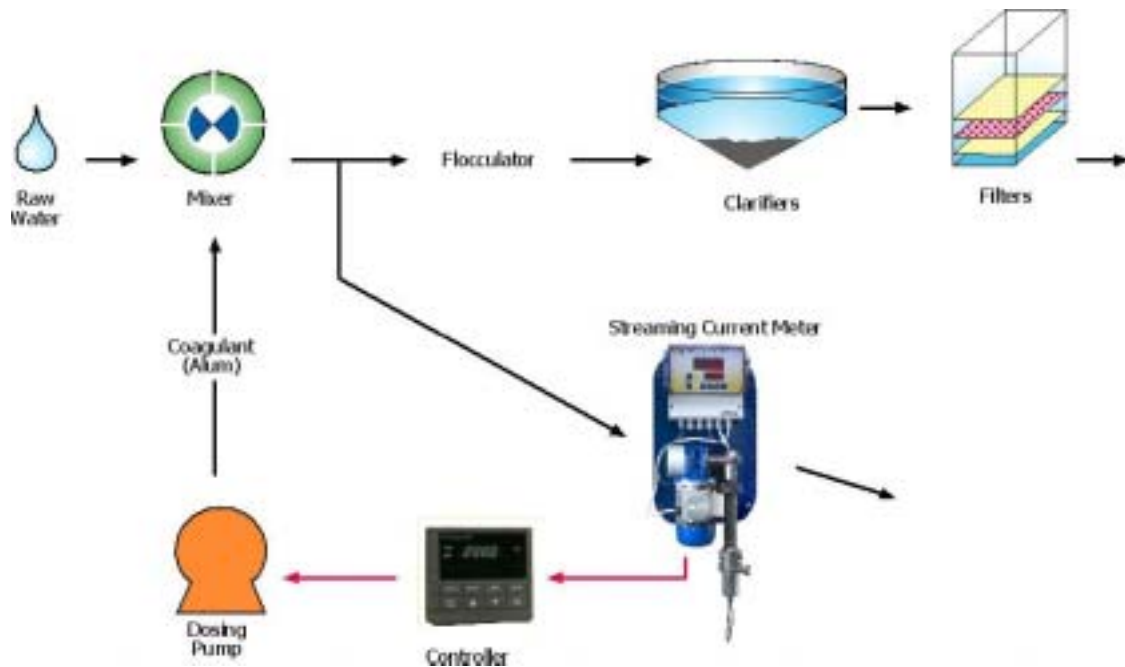
Figure 3 Diagram of SCM usage in a typical conventional plant.
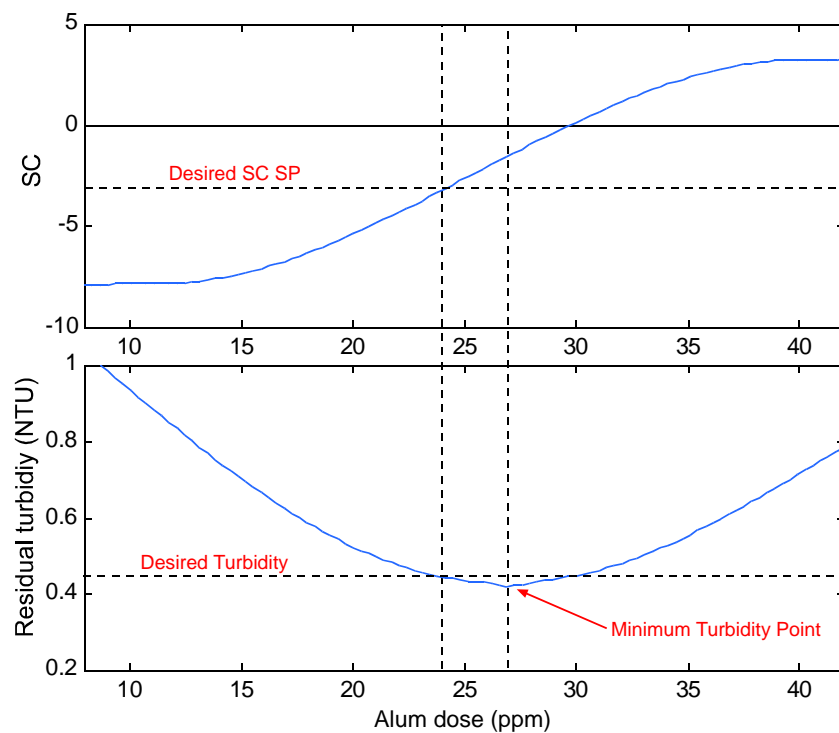
Figure 4 Typical relationship between alum, SC and settled water turbidity.

Caution and a lack of understanding kept the SCM from being used in most plants until the early 1980s. The study most widely cited, and credited with bringing widespread acceptance for use of the SCM in water treatment is the work of Dentel and Kingery (for a summary, see Dentel and Kingery 1989). This includes the result that SCM use resulted in generally improving water quality and consistency, as well as decreased chemical usage by 12% during stable operation and 23% during changing raw water conditions. A survey of plant's using an SCM showing 80% of them regarded it as useful. It is likely that these percentages would be higher today, even though many more SCMs are in use, due to better understanding by both users and manufacturers. One of the most common problems experienced is clogging of sample lines due to floc build-up. This can normally be minimised by use of an appropriate sample point and sampling design.

Another significant issue that has been widely identified since then is the effects of wear and tear on the measurement surfaces and the mechanisms. Any unevenness in the stroke due to misalignment or looseness in the mechanical drive will translate directly into a distortion of the SC signal. Changes in the condition of the sensing surfaces will change the manner in which they become coated with colloidal material and the equilibrium constants between the surfaces and the solution. These effects are normally the most significant on the surface of the piston. Once the wear reaches a certain level the reading produced becomes unstable, and commonly drifts in an unpredictable manner. It is not always possible to tell by inspection if a particular unit is in this condition.

The successful operation of a SCM has developed a (in the author's opinion, unjustified) reputation among some WTP operators for being more of an art than a science. The reasons include the difficulty in detecting failure, the arbitrary nature of the measured units and the inconsistency between different plants and different instruments.

However, the instrument's usefulness is no longer in question. For example, the New Zealand Ministry of Health requires plants supplying more than 5000 people to have automatic control of their coagulant dosage in order to achieve either of the highest 2 grades, required to be graded more than merely 'satisfactory' (Public Health Grading Drinking Water Supplies 2003). Currently, a SCM is the only technology that can provide this.

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