

**Review Article**

Entropy in the Brownian Motion (BM) and Coagulation Background

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Abstract: This review aims to highlight entropy in the Brownian motion (BM) and coagulation process background. In water treatment processes, pertinent questions relating to entropy, BM, and coagulation are often asked: Since entropy measures disorder of a system, does disorder manifest in polluted water with its stable colloids, microorganisms, molecules and ions? Are BM and molecular agitation favourable to separation processes? Since high salinity (as in seawater) decreases the disorder, would be increasing surface water salinity a convenient water treatment process? This review has found some links between entropy, BM, and coagulation such as: entropy is *neither 'disorder' nor* does it has anything to do with 'mixed-up things' like disorderly desks or shuffled cards. This review has also detailed the ordinary physical and chemical events whose spontaneity can be seen to be due to energy dispersing or spreading out. Coagulation/flocculation processes are employed to separate suspended solids from water whenever their natural subsidence rates are too slow to provide effective clarification. Adding salts to simply increase the ionic strength is almost never a practical option and other additives would be used; however, in seawater, where ionic strength is higher due to its proper dissolved salts, coagulation process is easier. Photovoltaically aided distillation process using large basins simulating sea open sky distillation process would be the *greenest* and healthiest water treatment technology.

Keywords: Entropy, Thermodynamics, Brownian Motion (BM), Coagulation, Water Treatment, Enhanced Coagulation (EC), Rapid Mixing (RM)

1. Introduction

In water treatment engineering [1-4], some basic questions are usually addressed: Does entropy [5-9] measure the disorder of a system? Does disorder manifest in polluted water with its suspended solids, colloidal particles, microorganisms, molecules and ions? Is it possible to measure water's (and raw water) entropy? Are Brownian motion (BM) [10] and molecular agitation favourable to separation processes? After coagulation/flocculation/settling processes [11, 12], two separated phases (limpid water + mud) are present: Does disorder is minimised? Does Freezing decrease disorder? Does freezing treat water? Does high salinity (as in seawater [4, 13]) decrease disorder? Is increasing surface water [14]

salinity a convenient water treatment process [2-4, 15]? In other words, this review aims to find some links between entropy, BM [10] and coagulation process [11, 16-20].

It is well-known that the most spectacular and crucial phenomenon of scientific advance is the expansion of thermodynamics since the 19th century [9, 21, 22]. Thermodynamics admitted the stochastic and probabilistic aspect of natural processes [9, 21, 23, 24]. It turned out that the doctrine of energy [25] and entropy rules the world: Energy is deterministic and entropy favours randomness. The chemical engineers became customary with the *entropy of mixing* which they employ to build phase diagrams [6-9, 26, 27].

On the other hand, coagulation/flocculation processes [11, 12] are largely used to separate suspended solids and dissolved

matters from water whenever their natural subsidence rates are too slow to provide effective clarification. For their efficiency, lime softening, sludge thickening, and dewatering depend on correct application of the theories of coagulation/flocculation [11, 12]. Coagulation/flocculation principles are highly related to rapid mixing (RM) of coagulants into water. This review tries to focus on entropy, BM and coagulation process.

2. Entropy

"A theory is the more impressive the greater the simplicity of its premises, the more varied the kinds of things that it relates and the more extended the area of its applicability. Therefore classical thermodynamics has made a deep impression on me. It is the only physical theory of universal content which I am convinced, within the areas of the applicability of its basic concepts, will never be overthrown." -- Einstein (1949) [7, 8, 21, 28].

The first law of thermodynamics affirms that *energy is conserved*. In other words, the total energy of a closed system should stay fixed. Since the universe is seen as a closed system, it possesses fixed energy. Energy is present in several types: as heat, kinetic (motion) energy, and potential (gravitational, electric, and magnetic) energy, etc. The energy may vary from one type to another. Nevertheless, the total energy of a closed system will always remain fixed. Energy may neither be created nor destroyed; it always goes elsewhere. The second law of thermodynamics announces that *the entropy of a closed system should always augment*. The *entropy* is an estimation of the system's disorder. If the universe may be seen itself as a closed system, in that case the entropy of the universe should always augment [5, 7-9, 21, 22, 29-34].

2.1. Temperature, Heat and Energy

Entropy is described in matter of temperature and heat [7]. Fahrenheit (1686-1736) [35] constructed the first thermometer which was precisely consistent and this made easy a systematic quantitative examination of temperature and heat. It appears to have been soon admitted that, when bodies at varying temperatures were placed into contact and when all changes had stopped, a thermometer brought in contact with each body in turn produced the same reading. This is a most crucial remark, so significant in fact that it has since been attributed the status of a law of thermodynamics – it is frequently named the *zeroth law* as the *first* and *second laws* of thermodynamics had already been formulated before this fact of observation was 'canonised'. At the time, nevertheless, this 'equilibrium of heat' – or thermal equilibrium as it must now be named – generated an important dubiety. As an illustration, it was explained to significate that at equilibrium there was an equal quantity of heat per unit volume across the different bodies. Joseph Black (1728-1799) [35] differentiated obviously between quantity and intensity of heat: in other words, between heat and temperature. He as well suggested the concepts of *heat capacity* and *latent heat*, and by his tests conducted to the basics of the *science of calorimetry* [7-9, 21, 27, 30, 35].

In addition, the term *energy* is a technical word proposed by Thomas Young (1773-1829) [26] in 1807. Its origin is the

Greek term *ἐνέργεια* which significates *efficacy* or *effective force*. Young employed it as an appropriate abbreviation for the sum of kinetic energy and gravitational potential energy of a mass and the elastic energy of a spring to which the mass may be fixed. That sum is conserved by Newton's laws and Hooke's law of elasticity, even if the individual contributions might vary. The word *energy* was not completely accepted until the second half of the 19th century when it was extrapolated away from mechanics to comprise the internal energy of thermodynamics and the electro-magnetic energy. Finally, in the early 20th century, energy was admitted as possessing mass, or being mass, following Einstein's formula $E = mc^2$, where c is the speed of light [7, 9, 21, 26].

2.2. Defining the Entropy

Entropy is defined in three varying yet equivalent manners [5, 28].

2.2.1. Probability

First we consider the probabilities for dice that every good backgammon players knows. In Table 1, the left column shows the sum of the two die; the next column lists all the possible combinations that give that sum; the third column counts the number of combinations for that sum. As it may be seen, there are a total of 36 various combinations for the two die, and each are equally probable to happen for "honest" dice. Therefore, the probability of getting a particular sum, as indicated in the last column, is just the number of combinations divided by 36. The most probable result, happening one-sixth of the time, is to get *seven*. The probabilities for dice conduct us to our first definition of the entropy: *the entropy is a measure of the probability of a particular result*. Here, then, a seven is the result with the highest entropy (i. e. probability), and a 2 ("snake eyes") or a 12 ("boxcars") have the lowest entropy. The entropy is actually $k_B \ln (\# \text{ combinations})$, where k_B is called *Boltzmann's constant* and \ln means the natural logarithm. Now we consider a "box" with two white marbles and two black marbles inside it (Figure 1). The box is made so that exactly two of the marbles are always on the left hand side and two are always on the right hand side of the box. In the case (a) of Figure 1, both white marbles are on the left side of the box and both black marbles are on the right side of the box. There is only one combination of marbles that gives this arrangement. Imagine that we shake the box, and how the marbles distribute themselves is random. Now we have a white marble and a black marble on the left, and a white and black marble on the right (case (b) of Figure 1). Call the black marbles B_1 and B_2 , and the white ones W_1 and W_2 . Then for this arrangement we could have B_1, W_1 on the left and B_2, W_2 on the right. We could also have B_1, W_2 on the left and B_2, W_1 on the right; or B_2, W_1 on the left and B_1, W_2 on the right; or B_2, W_2 on the left and B_1, W_1 on the right. Thus there are four combinations that give this arrangement of the marbles. Finally, we show the single arrangement with both black marbles on the left and both white ones on the right (case (c) of Figure 1). For the four marbles in a box that we just considered, there are a total of six

equally likely combinations. The one with the highest probability ($4/6 = 67\%$) has a black marble and a white marble on each side of the box. This is therefore the state with the highest entropy. The graph of Figure 2 shows the total number of combinations. For six marbles, three black and three white, the equivalent plot is shown in Figure 3. In Figure 4 we jump to a total of 12 marbles, six black and six white (here we did not find the number of combinations by brute force counting: we used some mathematics). In Figure 5 is the equivalent plot for a total of 100 marbles. The thing to notice is that the most probable result remains 50% black on the left, 50% black on the right, 50% white on the left and 50% white on the right. However, as the total number of marbles increases, the "peak" becomes sharper. This means that the probability of getting a result far away from 50% gets smaller and smaller the greater the number of marbles. You may wish to know that the total number of combinations for this case is about 1 followed by 29 zeroes before the decimal point. For a total of 400 marbles (Figure 6), the point we just made about the peak becoming narrower becomes even more obvious. Here the total number of combinations is about 1 followed by 119 zeroes before the decimal point. The conclusion from all this is that the most probable highest entropy result is the one in which equal numbers of white and black marbles occur on both sides of the box, and that as the total number of marbles increases the probability of getting a distribution very far from this most probable result goes down [28].

Table 1. Dice's probabilities [28].

Sum	Combinations	Number	Probability
2	1-1	1	$1/36 = 3\%$
3	1-2, 2-1	2	$2/36 = 6\%$
4	1-3, 3-1, 2-2	3	$3/36 = 8\%$
5	2-3, 3-2, 1-4, 4-1	4	$4/36 = 11\%$
6	2-4, 4-2, 1-5, 5-1, 3-3	5	$5/36 = 14\%$
7	3-4, 4-3, 2-5, 5-2, 1-6, 6-1	6	$6/36 = 17\%$
8	3-5, 5-3, 2-6, 6-2, 4-4	5	$5/36 = 14\%$
9	3-6, 6-3, 4-5, 5-4	4	$4/36 = 11\%$
10	4-6, 6-4, 5-5	3	$3/36 = 8\%$
11	5-6, 6-5	2	$2/36 = 6\%$
12	6-6	1	$1/36 = 3\%$

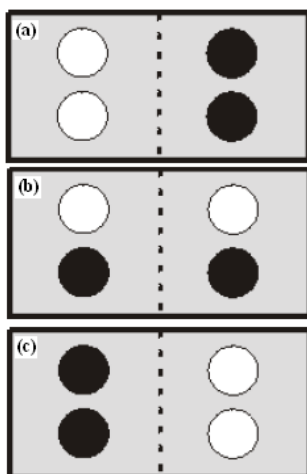


Figure 1. A "box" with two white marbles and two black marbles inside it [28].

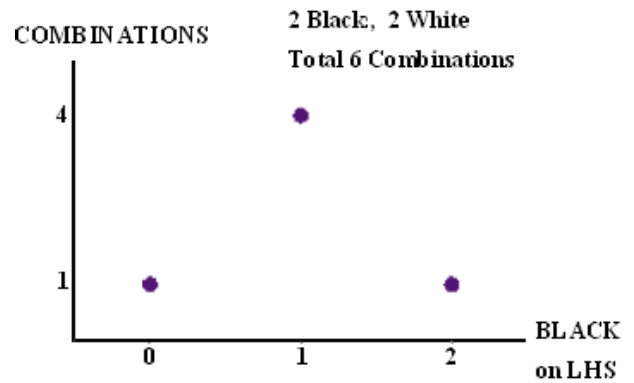


Figure 2. Total number of combinations of box with two white marbles and two black marbles inside it [28].

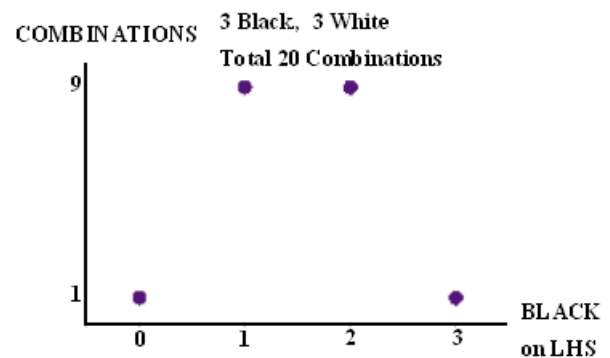


Figure 3. Total number of combinations of box with three white marbles and three black marbles inside it [28].

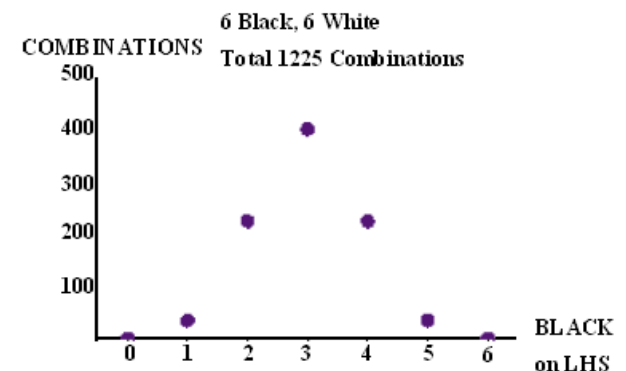


Figure 4. Total number of combinations of box with six white marbles and six black marbles inside it [28].

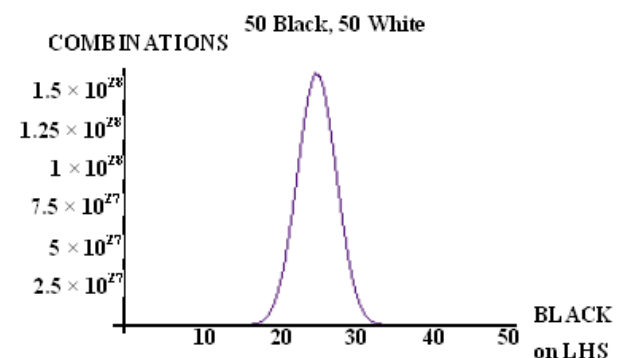


Figure 5. Total number of combinations of box with fifty white marbles and fifty black marbles inside it [28].

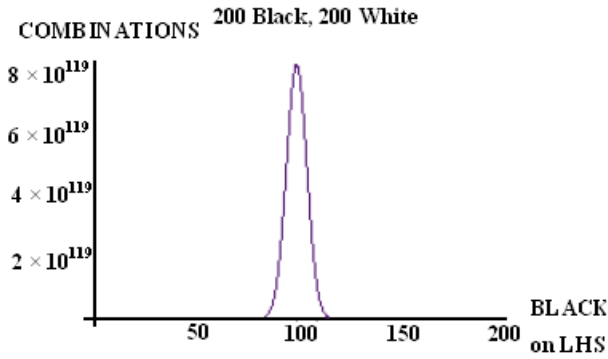


Figure 6. Total number of combinations of box with fifty white marbles and fifty black marbles inside it [28].

Further, entropy and probability are intrinsically related. Probability theory as logic may be applied to any field of science [36].

2.2.2. Disorder

Imagine the case above with a total of 200 black marbles and 200 white marbles. If all the white marbles are on the left hand side of the box and all the black ones are on the right hand side of the box, we say that the marbles are very ordered. If we have 100 black marbles on the left, 100 on the right, 100 white marbles on the left and 100 on the right, we say the system is very *disordered*, which is another way of saying that the two sides of the box are undifferentiated. Note that this is also the most probable state. Thus we are led to our second equivalent definition of entropy: *the entropy is a measure of the disorder of a system*. However, it is easy to get confused because this definition is the measure of the lack of order in a system. Usually we think of quantities such as mass, energy, etc. as measuring the amount of that something; here we are measuring the lack of that something. Some people like to talk about the *negentropy*, which is the negative of the entropy; it measures the order of the system [5, 7, 28].

2.2.3. Heat

Since $E = mc^2$, there is in fact a variation of mass of an object attributed to its heat even if not affected to the presence of caloric. This variation of mass, nevertheless, is basically immeasurable. As an illustration, if a 20 kg block of lead cools from 100 to 0°C, the variation of mass is around 3 *trillionths* of a kilogram. For the sake of completeness, we will as well consider the *absolute* temperature scale. It is well established experimentally that if we take a quantity of gas at constant volume and measure its pressure as a function of its temperature in, consider, Celsius, the relation will be a straight line (Figure 7). We may extrapolate that line back to the left to find the temperature when the pressure of the gas goes to zero. The result of the extrapolation is a temperature of -273.16 degrees. All gases exhibit this straight line relation between pressure and temperature. Moreover, if we do the extrapolation back to zero pressure, the result is -273.16 degrees for all gases. The phenomenon of pressure is attributed to the molecules of the gas bouncing off the walls of the container. Therefore, when the pressure has become zero

we have stopped the molecules from moving around; this is another manner of saying we have extracted all the heat from the object. Consequently, a temperature of -273.16 degrees is named *absolute zero*; it is the minimum temperature an object may possess. Therefore, nature seems to provide a temperature scale, which we call the *Kelvin* scale [28]:

$$T (\text{absolute, Kelvin}) = t (^{\circ}\text{C}) + 273.16 \quad (1)$$

Now, assume we have a system with 2 kinds of molecules:

1. High energy, hot molecules.
2. Low energy, cold molecules [7, 28].

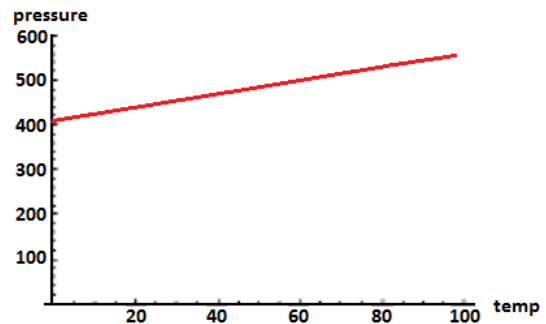


Figure 7. Gas pressure as a function of its temperature (Celsius) [28].

When the molecules collide a high energy molecule may transfer its energy to a low energy one. As a consequence, the energy may distribute itself in different fashions. The molecule-molecule collisions are basically random; thus, the manner the energy gets distributed is also random. Now, assume we have a total of four molecules in the system, two of them hot and two of them cold. Represent the hot molecules as white spheres and the cold ones as black spheres. Then, the manners the molecules may distribute themselves is exactly the same as the ways the four marbles, two black and two white, could distribute themselves in the first section above. In fact, *all* those somewhat dreary arguments about marbles can now be carried over to arguments about the distribution of heat in a body. We are now ready to state the third equivalent definition of the entropy: *the entropy measures the heat divided by the absolute temperature of a body*. We will be a bit mathematical (actually "arithmetical") to see how this definition works. Assume the left side of the body is at 273 Kelvin, and the right hand side is at 373 Kelvin. We will consider a small quantity of heat, say 0.001 Joules, being transferred either from the left to the right or the right to the left. We presume the quantity of heat is so small that the two sides of the body do not change their temperature [5, 7, 8, 28]:

1. Heat goes from the left to the right. The left hand side loses entropy by an amount of $0.001/273$; the right hand side gains entropy by an amount of $0.001/373$. The total change in entropy is $-0.001/273 + 0.001/373 = -0.000,000,98$; it decreases.
2. Heat goes from the right to the left. The left hand side gains entropy by an amount of $0.001/273$; the right hand side loses entropy by an amount of $0.001/373$. The total change is $+0.000,000,98$ [28].

Consequently, if the heat goes from the hotter right hand

side to the colder left hand side, the total system is moving to a state of higher entropy. This is also the state with the higher disorder, since the differentiation between the cold and hot sides is diminishing. It is also the state with the highest probability, since more combinations of hot and cold molecules make it up [28].

Moreover, a physicist likes to be able to grasp his concepts plausibly and on an intuitive level. In that respect, however, the entropy – for all its proven and recognised importance – is a disappointment. The formula $dS = dQ/T$ does not lend itself to a suggestive interpretation. What is required for the modern student of physics is an interpretation in terms of atoms and molecules. Like with temperature: it is all very well to explain that temperature is defined by its continuity at a diathermic wall, but the “ahaa”-experience comes only after it is clear that temperature measures the mean kinetic energy of the molecules and then it comes immediately. Such a molecular interpretation of entropy was missing in the work of Clausius. It arrived, however, with Boltzmann, although one must admit, that the interpretation of entropy was considerable more subtle than that of temperature [7, 26].

2.3. The Second Law of Thermodynamics

In the previous section we developed three equivalent definitions of entropy:

1. The entropy is a measure of the probability of a particular result.
2. The entropy is a measure of the disorder of a system.
3. The entropy measures the heat divided by the absolute temperature of a body [5, 7-9, 21, 28, 30].

Regardless of which definition is used, the second law of thermodynamics states: *The entropy of a closed system “never” decreases.* A common statement of the law is: “The heat never flows from the colder to the hotter.” We have just seen in the previous section how the “official” form of the second law plus definition three for the entropy is consistent with this common statement. Consider your refrigerator. It takes heat from the cold interior and deposits it in the warmer air of your kitchen via the coils on the back of the fridge. Does this violate the second law? No, because of the phrase *closed system* in the law. Even if the door is closed your fridge is not a closed system; it is connected to an outside power source via the cord plugged into the electrical outlet. Unplug your fridge and the heat will start moving from your kitchen into the fridge, spoiling the food [5, 7, 9, 21, 28, 30].

We have just considered the third definition of entropy.

Continuing to explore the list in reverse order, one implication of the second definition is that the second law says that the universe is turning into *kibble*. Another way of saying this is that if the universe is *open* then eventually it will be one with no differentiation: all parts will be of equal temperature. We will explore the consequences if the universe is *closed* soon. Finally, the first definition of entropy reads that the less probable result never happens. This is not quite correct. Imagine the air molecules in a room: there is a non-zero probability that all the molecules will rush into the far corner of the room and we will all suffocate. But, as we have seen, if the number of molecules in the room is sufficiently large the probability is very small. The number of molecules in a typical room is about 1 followed by 80 zeroes before the decimal point. So, the probability is so small that we, erroneously, say it can never happen. This is why we put the word “never” in quotation marks in the “official” statement of the second law of thermodynamics; to be completely correct we should have said “usually” [5, 8, 9, 21, 28, 30].

Moreover, the second law originated from human experience with thermal energy, not from abstract theory [7, 8, 21, 30, 37, 38].

2.4. Entropy and the Environment

Philosophically, several of our environmental issues are characterised by large augmentations in entropy in the nature [7]. It is because these variations are irreversible that our society is unsustainable. We extract natural resources to generate goods, and when they are worn out we throw them away and start again. We don’t commonly re-use those resources, which are now dispersed through landfill sites or incineration. These are high entropy systems that would require high energy input to reclaim the materials. In the process we rely on the throughput of large amounts of non-renewable energy [7].

In several fashions, mankind’s interaction with Earth is to turn a highly complex, diverse system (low entropy) into a much simpler degraded environment (high entropy), in a manner that is basically irreversible due to the augmentations in entropy taking place. The natural systems are sustainable because they are reliant only on the energy from the Sun to maintain their low entropy, while we have increased the energy throughput by using fossil fuels. In the process we are creating our own very complex physical and social environment which has low entropy, but is dependent upon these energy flows, and on degradation of natural systems (Table 2) [7].

Table 2. Environmental issues and entropy [7].

Low entropy state	Higher entropy state
Fossil energy resources in concentrated form underground.	Energy degraded to heat; resources reduced to CO ₂ and dispersed through the atmosphere.
Minerals and metals in concentrated form underground.	Minerals and metals dispersed through mine waste and final disposal of goods after consumption, energy used in processing.
Land covered by highly diverse ecosystems with many species.	Much land in monoculture agriculture sustained by high energy input, many species extinct.
Surface waters kept pure by balance of biological and physical systems.	Rivers and oceans polluted by low concentrations of many toxic and carcinogenic substances.
Soils developed over a long time, containing a balanced community of animal, plant and bacterial life.	Soils reduced by pesticides/herbicides to an inorganic substrate needing energy-intensive artificial fertilisers to be productive, or damaged by erosion.

As a consequence, entropy is augmenting much faster. Much of environmental awareness concerns recognizing this phenomenon, and taking adequate decisions concerning whether what we are destroying is a price worth paying for the material world we are creating [7].

3. Brownian Motion (BM)

3.1. Defining BM

BM is observed in suspensions of tiny particles which follow irregular, erratic paths visible under the microscope [10]. The phenomenon was reported by Robert Brown (1773–1858) in 1828 [39]. He was not the first person to observe this, but he was first to recognise that he was not seeing some kind of self-animated biological movement. He proved the point by observing suspensions of organic *and* inorganic particles. Among the latter category there were *ground-up fragments of the Sphinx*, surely a dead substance, if ever there was one. All samples showed the same behaviour and no convincing explanation or description could be given for nearly 80 years [26].

After the kinetic theory of gases was proposed and slowly accepted, the impression grew that the phenomenon provides a *beautiful and direct experimental demonstration of the fundamental principles of the mechanical theory of heat*. That interpretation was supported by the observation that at higher temperatures the motion becomes more rapid. However, none of the protagonists of the field of kinetic theory addressed the problem, neither Clausius, nor Maxwell, nor Boltzmann. It may be that they did not wish to become involved in liquids. A great difficulty was that the Brownian particles were about 10^8 times more massive than the molecules of the solvent so that it seemed inconceivable that they could be made to move appreciably by impacting molecules [10, 26].

It was Poincaré – the mathematician who enriched the early history of thermodynamics on several occasions with his perspicacious remarks – who identified the mechanism of BM [10, 21] when he said:

“Bodies too large, those, for example, which are a tenth of a millimetre, are hit from all sides by moving atoms, but they do not budge, because these shocks are very numerous and the law of chance makes them compensate each other; but the smaller particles receive too few shocks for this compensation to take place with certainty and are incessantly knocked about.” Also Poincaré noted that the existence of BM [10] was in contradiction to the second law of thermodynamics when he said:

... “but we see under our eyes now motion transformed into heat by friction, now heat changed inversely into motion, and [all] that without loss, since the movement lasts forever. This is the contrary of the principle of Carnot.” And indeed, the existence of BM demonstrates that the second law is a law of probabilities. It cannot be expected to be valid when few particles or few collisions are involved. If that is the case, there will be sizable fluctuations around equilibrium [7, 10, 26, 30].

3.2. Brownian Motion (BM) as a Stochastic Process

And so we come to the third one of Einstein’s seminal papers of the annus mirabilis: “On the movement of small particles suspended in a stationary liquid demanded by the molecular-kinetic theory of heat.” After Poincaré’s remarks the physical explanation of the BM was known, but what remained to be done was the mathematical description. Actually Einstein claimed to have provided both: The physical explanation and the mathematical formulation. As a matter of fact, he even claimed to have foreseen the phenomenon on general grounds, without knowing of BM at all [10, 24, 26].

Indeed, in his doctoral dissertation, submitted to the University of Zurich in 1905, Einstein developed a statistical molecular theory of liquids. Then, in a separate paper, he applied the molecular theory of heat to liquids in obtaining an explanation of what had been, unknown to Einstein, a decades-old puzzle. Observing microscopic bits of plant pollen suspended in still water, Robert Brown had noticed (in 1828) that the pollen seeds exhibited an incessant, irregular “swarming” motion, since called “Brownian motion (BM)” [10]. Although atoms and molecules were still open to objection in 1905, Einstein predicted that the random motions of molecules in a liquid impacting on larger suspended particles—such as pollen seeds—would result in irregular, random motions (Figure 8) of the particles, which could be directly observed under a microscope. The predicted motion corresponded precisely with the puzzling BM! From this motion Einstein accurately determined the dimensions of the hypothetical molecules. By 1908 the molecules could no longer be considered hypothetical. The evidence gleaned from BM on the basis of Einstein’s work was so compelling that Mach, Ostwald, and their followers were thrown into retreat, and material atoms soon became a permanent fixture of our knowledge of the physical world. Today, with the advent of scanning tunnelling microscopes, scientists are nearly able to see and even to manipulate actual, individual atoms for the first time [10, 39].

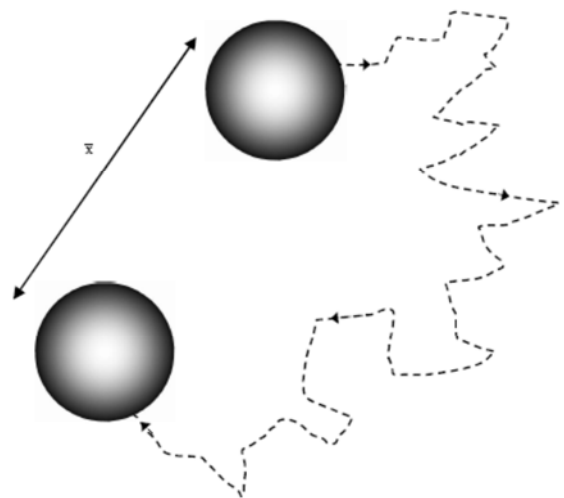


Figure 8. Showing a typical “random walk” in two dimensions. In a given time, the particle moves, on average, a distance x from its starting position [40].

4. Collision Mechanisms

The only significant ways in which particles are brought into contact are as follows:

1. Brownian diffusion (*perikinetic* aggregation) [10].
2. Fluid motion (*orthokinetic* aggregation) [10].
3. Differential sedimentation [40].

These are shown schematically in Figure 9. We saw previously that all particles in water [41] undergo random movement as a result of their thermal energy and that this is known as *Brownian motion* (BM) [10]. For this reason, collisions between particles will occur from time to time, giving *perikinetic aggregation*. It is not difficult to calculate the collision frequency. It is obvious that Brownian (perikinetic) aggregation [10] does not easily lead to the formation of large aggregates because of the reduction in particle concentration and the second-order nature of the process. In practice, aggregation (flocculation) processes are nearly always carried out under conditions where the suspension undergoes some form of *shear*, such as by stirring or flow. Particle transport by fluid motion can have an enormous effect on the rate of particle collision, and the process is known as *orthokinetic aggregation*. The first theoretical approach to this was also the result of Smoluchowski's work, alongside his pioneering work on perikinetic aggregation. For orthokinetic collisions, he considered the case of spherical particles in *uniform, laminar shear*. Such conditions are never encountered in practice, but the simple case makes a convenient starting point. Figure 10 shows the basic model for the Smoluchowski treatment of orthokinetic collision rates. Two spherical particles, of different size, are located in a uniform shear field. This means that the fluid velocity varies linearly with distance in only one direction, perpendicular to the direction of flow. The rate of change of fluid velocity in the z -direction is du/dz . This is the *shear rate* and is given the symbol G . The centre of one particle, radius a_j , is imagined to be located in a plane where the fluid velocity is zero, and particles above and below this plane move along fluid streamlines with different velocities, depending on their position. A particle of radius a_i will *just* contact the central sphere if its centre lies on a streamline at a distance $a_i + a_j$ from the plane where $u = 0$ ($a_i + a_j$ is the *collision radius*, as in the treatment of perikinetic aggregation). All particles at distances less than the collision radius will collide with the central sphere, at rates that depend on their concentration and position (and hence velocity) [40].

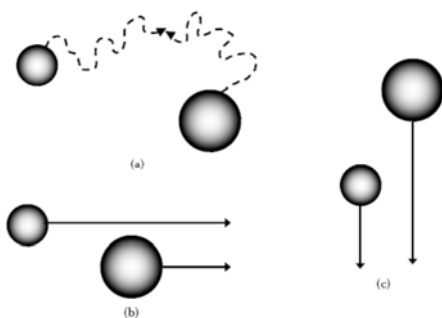


Figure 9. Particle transport leading to collisions by (a) Brownian diffusion, (b) fluid motion, and (c) differential sedimentation [40].

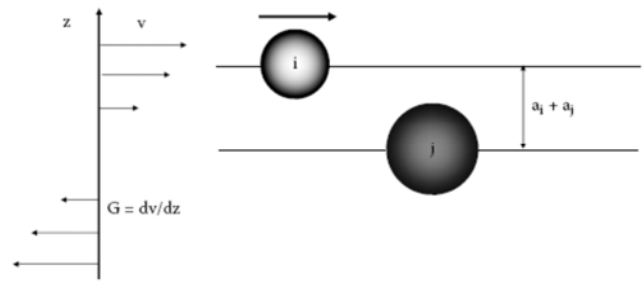


Figure 10. Model for orthokinetic aggregation in uniform laminar shear [40].

Another important collision mechanism arises whenever particles of different size or density are settling from a suspension. Larger and denser particles will sediment faster and can collide with more slowly settling particles as they fall [40].

5. Colloids

Colloids are agglomerates of atoms or molecules whose sizes are so small that gravity has no effect on settling them but, instead, they stay in suspension. Because they stay in suspension, they are said to be stable. The reason for this stability is the mutual repulsion between colloidal particles. They may, however, be destabilised by application of chemicals. *Coagulation* is the unit process [11, 12, 42, 43] of applying these chemicals for the purpose of destabilising the mutual repulsion of the particles, thus causing the particles to bind together. This process is normally applied in conjunction with the unit operation of flocculation [44]. The colloidal particles are the cause of the turbidity and colour that make waters objectionable, thus, should, at least, be partially removed [38].

This section discusses prerequisite topics necessary for the understanding of coagulation [11, 45] such as the behaviour of colloids, zeta potential [46], and colloid stability [11, 38].

5.1. Colloid Behaviour

Much of the suspended matter in natural waters is composed of silica, or similar materials, with specific gravity of 2.65. In sizes of 0.1 to 2 mm, they settle rapidly; however, in the range of the order of 10^{-5} mm, it takes them a year, in the overall, to settle a distance of only 1 mm. And, yet, it is the particle of this size range that causes the turbidity and colour of water, making the water objectionable. The removal of particles by settling is practical only if they settle rapidly in the order of several hundreds of millimetres per hour. This is where coagulation [11, 12] can perform its function, by destabilising the mutual repulsions of colloidal particles causing them to bind together and grow in size for effective settling. Colloidal particles fall in the size range of 10^{-6} mm to 10^{-3} mm. They are aggregates of several hundreds of atoms or molecules, although a single molecule such as those of proteins is enough to be become a colloid. The term colloid comes from the two Greek words *kolla*, meaning glue, and *eidos* meaning like [38].

A colloid system is composed of two phases: the *dispersed*

phase, or the *solute*, and the *dispersion medium*, or the *solvent*. Both of these phases can have all three states of matter which are solid, liquid, and gas. For example, the dispersion medium may be a liquid and the dispersed phase may be a solid. This system is called a *liquid sol*, an example of which is the turbidity in water. The dispersion medium may be a gas and dispersed phase may be solid. This system is called a *gaseous sol*, and examples are dust and smoke. Table 3 shows the different types of colloidal systems. Note that it is not possible to have a colloidal system of gas in a gas, because gases are completely soluble in each other. In the coagulation treatment [11, 12] of water and wastewater [43, 47], we will be mainly interested in the solid being dispersed in water, the liquid sol or simply sol. Unless required for clarity, we will use the word “sol” to mean liquid sol. Sols are either *lyophilic* or *lyophobic*. Lyophilic sols are those that bind the solvent, while the lyophobic sols are those that do not bind the solvent. When the solvent is water, lyophilic and lyophobic sols are, respectively,

called *hydrophilic* and *hydrophobic sols* [12]. The affinity of the *hydrophilic sols* for water is due to polar functional groups that exist on their surfaces [12]. These groups include such polar groups as $-\text{OH}$, $-\text{COOH}$, and $-\text{NH}_2$. They are, respectively, called the *hydroxyl*, *carboxylic*, and *amine* groups. Figure 11 (a) shows the schematic of a hydrophilic colloid [12]. As portrayed, the functional polar groups are shown sticking out from the surface of the particle. Because of the affinity of these groups for water, the water is held tight on the surface. This water is called *bound water* and is fixed on the surface and moves with the particle. The *hydrophobic colloids* do not have affinity for water; thus, they do not contain any bound water. In general, inorganic colloids are hydrophobic, while organic colloids are hydrophilic [12]. An example of an inorganic colloid is the clay particles that cause turbidity in natural water, and an example of an organic colloid is the colloidal particles in domestic sewage [38, 48].

Table 3. Types of colloidal systems [38].

Dispersion Medium	Dispersed Phase	Common Name	Example
Solid	Solid	Solid sol	Coloured glass and gems, some alloys
Solid	Liquid	Solid emulsion	Jelly, gel, opal (SiO_2 and H_2O), pearl (CaCO_3 and H_2O)
Solid	Gas	None	Pumice, floating soap
Liquid	Solid	Liquid sol	Turbidity in water, starch suspension, ink, paint, milk of magnesia
Liquid	Gas	Foam	Whipped cream, beaten egg whites
Gas	Solid	Gaseous sol	Dust, smoke
Gas	Liquid	Gaseous emulsion	Mist, fog, cloud, spray
Gas	Gas	Not applicable	None

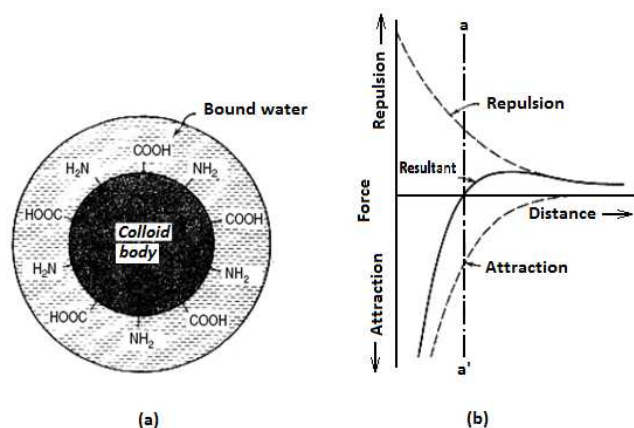


Figure 11. (a) Hydrophilic colloid encased in bound water; (b) interparticle forces as a function of interparticle distance [38].

5.2. Zeta Potential

The repulsive property of colloidal particles is due to electrical forces that they possess. The characteristic of these forces is indicated in the upper half of Figure 11 (b). At a short distance from the surface of the particle, the force is very high. It dwindles down to zero at infinite distance from the surface. The electrical forces are produced due to the charges that the particles possess at their surfaces. These charges called *primary charges* are, in turn, produced from one or both of two phenomena: the dissociation of the polar groups and preferential adsorption of ions from the dispersion medium.

The primary charges on hydrophobic colloids are due to preferential adsorption of ions from the dispersion medium [12, 38].

The primary charges on hydrophilic colloids are due chiefly to the polar groups such as the carboxylic and amine groups [12]. The process by which the charges on these types of colloids are produced is indicated in Figure 12. The symbol R represents the colloid body. First, the colloid is represented at the top of the drawing, without the effect of pH. Then by a proper combination of the H^+ and OH^- being added to the solution, the colloid attains ionisation of both carboxylic and the amine groups. At this point, both ionised groups neutralise each other and the particle is neutral. This point is called the *isoelectric point*, and the corresponding ion of the colloid is called the *zwitter ion*. Increasing the pH by adding a base causes the added OH^- to neutralise the acid end of the zwitter ion (the NH_3^+); the zwitter ion disappears, and the whole particle becomes negatively charged. The reverse is true when the pH is reduced by the addition of an acid. The added H^+ neutralises the base end of the zwitter ion (the COO^-); the zwitter ion disappears, and the whole particle becomes positively charged. From this discussion, a hydrophilic colloid can attain a primary charge of either negative or positive depending upon the pH [12]. The primary charges on a colloid which, as we have seen, could either be positive or negative, attract ions of opposite charges from the solution. These opposite charges are called *counterions*. This is indicated in Figure 13. If the primary charges are sufficiently large, the attracted counterions can form a compact layer around the

primary charges. This layer is called the *Stern layer*. The counterions, in turn, can attract their own counterions, the *coions* of the primary charges, forming another layer. Since these coions form a continuous distribution of ions into the bulk of the solution, they tend to be diffused and form a diffused layer. The second layer is called the *Gouy layer*. Thus, the *Stern* and *Gouy* layers form an envelope of electric double layer around the primary charges. All of the charges in the Stern layer move with the colloid; thus, this layer is a fixed layer. In the Gouy layer, part of the layer may move with the colloidal particle by shearing at a *shear plane*. This layer may shear off beyond the boundary of the fixed Stern layer measured from the surface of the colloid. Thus, some of the charges in the layer move with the particle, while others do not. This plane is indicated in Figure 13 [38].

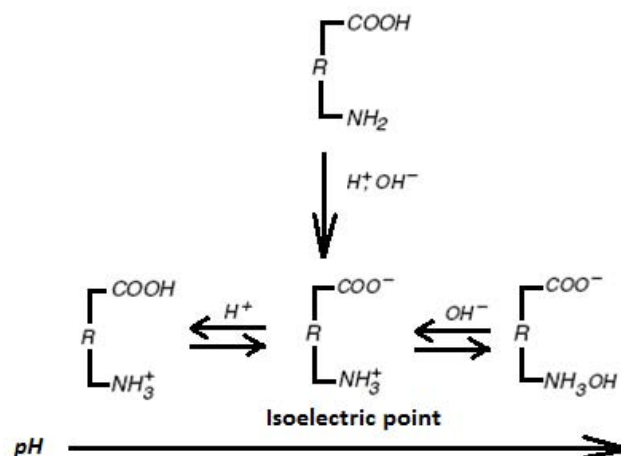


Figure 12. Primary charges of a hydrophilic colloid as a function of pH [38].

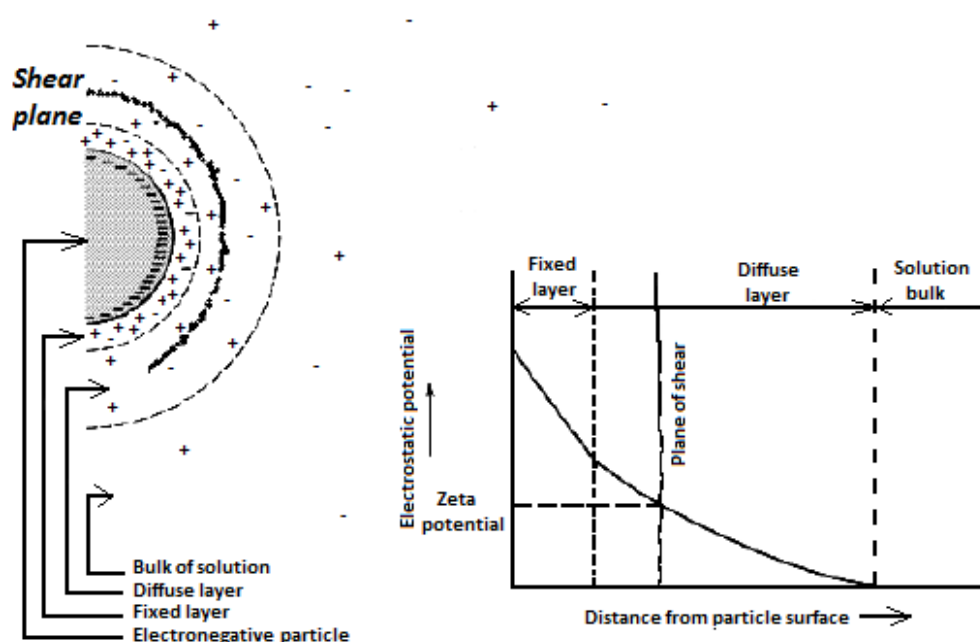


Figure 13. Charged double layer around a negatively charged colloid (left) and variation of electrostatic potential with distance from particle surface (right) [38].

The charges are electric, so they possess electrostatic potential. As indicated on the right-hand side of Figure 13, this potential is greatest at the surface and decreases to zero at the bulk of the solution. The potential at a distance from the surface at the location of the shear plane is called the *zeta potential* [46]. Zeta potential meters are calibrated to read the value of this potential. The greater this potential, the greater is the force of repulsion and the more stable the colloid [38, 46].

5.3. Colloid Destabilisation

Colloid stability may further be investigated by the use of Figure 11 (b). Figure 11 (b) portrays the competition between two forces at the surface of the colloidal particle: the *van der Waal's force of attraction*, represented by the lower dashed curve, and the force of repulsion, represented by the upper dashed curve. The solid curve represents the resultant of these two forces [49]. As shown, this resultant becomes zero

at $a - a'$ and becomes fully an attractive force to the left of the line. When the resultant force becomes fully attractive, two colloidal particles can bind themselves together. The force of repulsion, as we have seen, is due to the charges on the surface. Inherent in any body is a natural force that tends to bind particles together. This force is exactly the same as the force that causes adsorption of particles to an adsorbing surface. This is caused by the imbalance of atomic forces on the surface. Whereas atoms below the surface of a particle are balanced with respect to forces of neighbouring atoms, those at the surface are not. Thus, the unbalanced force at the surface becomes the van der Waal's force of attraction. By the presence of the primary charges that exert the repulsive force, however, the van der Waal's force of attraction is nullified until a certain distance designated by $a - a'$ is reached. The distance can be shortened by destabilising the colloidal particle [38]. The use of chemicals to reduce the

distance to $a - a'$ from the surface of the colloid is portrayed in Figure 14. The zeta potential is the measure of the stability of colloids [46]. To destabilise a colloid, its zeta potential [46] must be reduced; this reduction is equivalent to the shortening of the distance to $a - a'$ and can be accomplished through the addition of chemicals. The chemicals to be added should be the counterions of the primary charges. Upon addition, these counterions will neutralise the primary charges reducing the zeta potential [46]. This process of reduction is indicated in Figures 14 (a) and 14 (b); the potential is reduced in going from Figure 14 (a) to Figure 14 (b). Note that destabilisation is simply the neutralisation of the primary charges, thus reducing the force of repulsion between particles. The process is not yet the *coagulation* of the colloid [11, 12, 38].

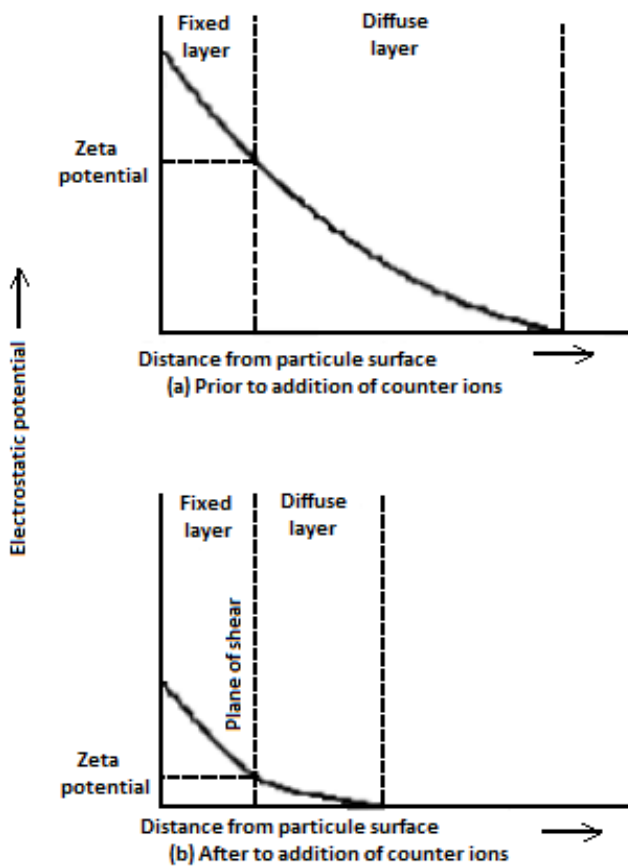


Figure 14. Reduction of zeta potential to cause destabilisation of colloids [38].

6. Coagulation and Flocculation

6.1. Terminology

6.1.1. “Coagulation” and “Flocculation”

This section is concerned with processes in which small particles in water form larger aggregates that can be more easily removed by physical separation processes such as sedimentation, flotation, and filtration [11]. Assuming that the particles are initially stable in the colloidal sense, and then there are two essential steps in the aggregation process, which

are shown schematically in Figure 15:

1. Destabilisation of particles
2. Collisions of particles to form aggregates [40].

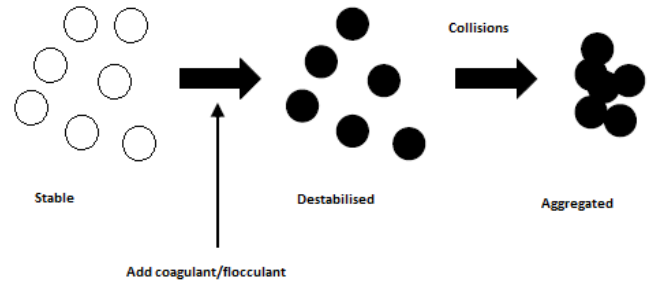


Figure 15. Destabilisation and aggregation of particles [40].

We will be dealing mainly with particles that are stable by virtue of their surface charge and hence electrical double-layer repulsion. In that case, destabilisation involves either an increase in ionic strength or a neutralisation of the particle charge. Adding salts simply to increase ionic strength is almost never a practical option and other additives have to be used, as described later in this section. The purpose of the destabilisation step is to make the *collision efficiency*, α , as high as possible, ideally with $\alpha = 1$, so that every collision leads to aggregation. Even when particles are fully destabilised, so that $\alpha = 1$, collisions are essential if aggregates are to be formed. The particle collision frequency is greatly dependent on the particle concentration and on the collision mechanism. For dilute dispersions, where the collision frequency may be very low, it is possible for particles to be fully destabilised but to show very little aggregation over appreciable time scales. Because of the short-range nature of colloidal interactions, it is usually possible to treat the destabilisation and collision processes as independent. In other words, it is nearly always safe to assume that the collision frequency is not affected by colloid interactions [40].

So far in this review, the term “aggregation” has been used in a generic sense, to mean any process whereby particles cluster together to form larger units. It is now time to address the question of other terminology, in particular the widely used terms *coagulation* and *flocculation* [11, 12, 50]. Unfortunately there is no general agreement on how these terms should be used and there are at least two conventions in widespread use [11, 40].

In the colloid science community it is common to restrict the term *coagulation* to cases where particles are destabilised by simple salts or by charge neutralisation and the aggregates (*coagula*) tend to be small and dense. *Flocculation* is then restricted to the cases where polymer bridging [11, 12, 51] is the dominant mechanism and aggregates (*flocs*) tend to be larger and more open in structure. Because of the fractal nature of aggregates it is natural that larger structures tend to be more open and less dense. So the distinction between small, compact coagula and larger, less dense flocs is an inevitable consequence of the stronger interparticle binding in the case of polymers, leading to larger aggregates. Another complication is that *flocculation* is sometimes applied to cases where

aggregation occurs in a *secondary minimum*. Another, quite different convention is commonly used in the area of water and wastewater treatment [2-4, 15, 43, 52]. According to this usage, *coagulation* [11, 12, 43, 53, 54] refers to destabilisation, by the dosing of appropriate additives, and *flocculation* implies the formation of aggregates, usually by some form of fluid motion (i. e., orthokinetic aggregation). These correspond to the two stages in Figure 15 and could be regarded as chemical and physical aspects of the aggregation process [40].

6.1.2. Destabilising Agents

Because of the first distinction drawn between coagulation and flocculation [11, 12, 55], the additives used to cause destabilisation of colloids may be called *coagulants* or *flocculants*, depending on their mode of action. Coagulants would then be inorganic salts, including those containing specifically adsorbing counterions, and flocculants would be long-chain polymers, which give bridging interactions. Although there are potentially many different kinds of destabilising agents, the vast majority of those used in practice fall into one of just two categories:

1. Hydrolysing metal coagulants
2. Polymeric flocculants [40, 56].

The nature of these materials and their mode of action will be discussed in the following sections [40].

6.2. Hydrolysing Metal Coagulants

The most widely used coagulants are based on aluminium [57, 58] and ferric salts, such as aluminium sulphate ("alum") [59] and ferric chloride. Originally, it was thought that their action was a result of the trivalent nature of the metals, giving Al^{3+} and Fe^{3+} ions in solution, which are expected to be very effective in destabilising negatively charged colloids. However, this is a greatly oversimplified view because trivalent metal ions are readily *hydrolysed* in water, which has an enormous effect on their behaviour as coagulants [40].

6.2.1. Hydrolysis of Metal Cations

In some cases, metal ions in water exist mainly in the form of simple hydrated cations. This is the case for alkali metal ions such as Na^+ and K^+ . Because of the polar nature of water, such cations are *hydrated* to some extent, which means they are surrounded by a certain number of water molecules held by electrostatic attraction between the positive metal ion and the negative (oxygen) ends of the water molecules. It is reasonable to think in terms of a *primary hydration shell*, where water molecules are in direct contact with the central metal ion and more loosely held water in a secondary hydration shell. In the case of the trivalent metal ions Al^{3+} and Fe^{3+} it is known that the primary hydration shell consists of six water molecules in octahedral coordination, as shown in Figure 16 (a). Now, because of the high positive charge on the central metal ion, there is a tendency for electrons to be drawn toward the metal from the water molecules, and this can lead to the dissociation of a proton, H^+ , leaving a hydroxyl group attached and a reduced positive charge for the metal, as shown

in Figure 16 (b). Because the process essentially involves the splitting of water molecules, it is known as *hydrolysis*. Because hydrolysis causes the release of a hydrogen ion into solution, it is greatly dependent on the pH. High pH values promote dissociation and vice versa. Furthermore, as each proton is released, the decreasing positive charge makes further dissociation more difficult. It follows that with increasing pH there is a sequence of hydrolysis equilibria, which can be written as follows [40]:

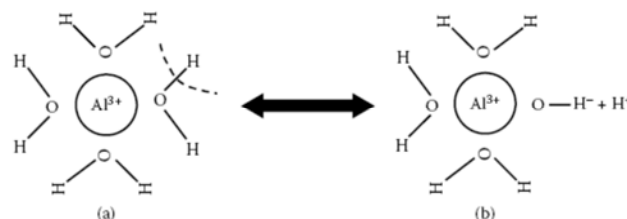
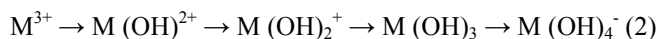
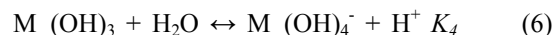
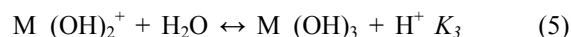
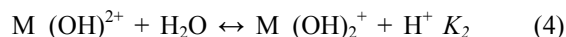
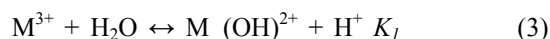


Figure 16. Hydrolysis of Al^{3+} [(a) hydrated aluminium cation, only 4 of 6 water molecules shown, (b) after loss of H^+ to give $\text{Al}(\text{OH})^{2+}$] [40].

For simplicity, water molecules in the hydration shell are omitted. Each of the stages in the hydrolysis process has an appropriate equilibrium constant [40]:

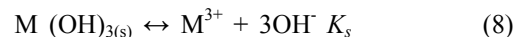


These are defined in the conventional manner, so that in the case of K_2 , for example:

$$K_2 = \frac{[\text{M}(\text{OH})_2^+][\text{H}^+]}{[\text{M}(\text{OH})^{2+}]} \quad (7)$$

where square brackets indicate molar concentrations of the various species [40].

For Al and Fe (III), the uncharged hydroxide, $\text{M}(\text{OH})_3$, has very low solubility in water and is likely to form a precipitate over a certain range of pH. This precipitation is of great importance in the action of hydrolysing metal coagulants. As well as the equilibrium constants listed earlier, a solubility constant for the metal hydroxide is also needed, based on the following dissolution of the solid phase, $\text{M}(\text{OH})_{3(s)}$:



$$K_s = [\text{M}^{3+}][\text{OH}^-]^3 \quad (9)$$

If true equilibrium were attained, then the appropriate solubility constants would be those for the stable crystalline forms such as gibbsite and goethite, in the case of Al and Fe, respectively. However, these are usually formed slowly (usually weeks or months). From the standpoint of coagulation processes [11, 17-20] it is much more relevant to

consider the solubility constants (K_{sam}) of the amorphous precipitates that form initially. Unfortunately these values are subject to some uncertainty and only estimated values can be given. They are usually at least 100-fold larger than values for the corresponding crystalline solids, so that the amorphous material is effectively much more soluble. Table 4 gives some values for the hydrolysis and solubility constants for Al and Fe (III) species in water at 25°C and at zero ionic strength, so they are appropriate for low salt concentrations, typical of many natural waters. The constants are given in the conventional pK form (where $pK = -\log_{10}K$). Using these pK values, it is possible to calculate, as a function of pH, the concentrations of the various dissolved hydrolysis products in equilibrium with the amorphous hydroxide precipitate. Because of uncertainties over the solubility constants for the amorphous precipitates, the results may not be completely reliable, but they give a useful indication of the relative importance of the different species over a range of pH values. Figure 17 is a *speciation* diagram showing the results of such calculations for Al and Fe (III), based on the values in Table 4. The total concentration of dissolved species in equilibrium with the amorphous precipitate is effectively the solubility of the metal at a given pH value. It is evident from Figure 17 that there is a minimum solubility that occurs around neutral pH for both metals. Note that the minimum solubility of Fe (III) is much lower than that of Al and that the minimum is considerably broader. It is also apparent that, in the case of Al, the anionic form $Al(OH)_4^-$ (aluminate) [58] is the dominant dissolved species above neutral pH. Another way of showing the speciation data is to plot the mole fraction of each species in

relation to the total dissolved amount in equilibrium with the amorphous hydroxide. This has been done in Figure 18 for Al and Fe (III). These results show considerable differences between the two metals. In the case of Al, the predominant species are the trivalent ion, Al^{3+} , at low pH (up to about 4.5) and the aluminate ion, $Al(OH)_4^-$, at pH values higher than about 7. The intermediate species make only minor contributions at pH values in the region of about 4–6.5. For Fe (III) the various species are spread over a much broader pH range (about 8 units) and each hydrolysis product is dominant at some pH values. This is the expected behaviour for hydrolysis of metal ions. The reason that Al species are “squeezed” into a much narrower pH range is believed to be the result of a transition from octahedral coordination in $Al^{3+} \cdot 6H_2O$ to the tetrahedral $Al(OH)_4^-$. In the case of Fe (III), octahedral coordination is maintained throughout. It is also worth noting that the *soluble*, uncharged $Fe(OH)_3$ is the predominant dissolved Fe species in the pH range 7–9 (although the actual concentration is only around 2×10^{-8} M). The corresponding Al species, $Al(OH)_3$, is always a minor dissolved component in *relative* terms, although it is at least 10 times more soluble than $Fe(OH)_3$ [40].

Table 4. Equilibrium constants (pK values) for Al and Fe (III) hydrolysis and solubility of amorphous hydroxides (values for 25°C and zero ionic strength) [40].

	pK_1	pK_2	pK_3	pK_4	pK_{sam}
Al^{3+}	4.95	5.6	6.7	5.6	31.5
Fe^{3+}	2.2	3.5	6	10	38

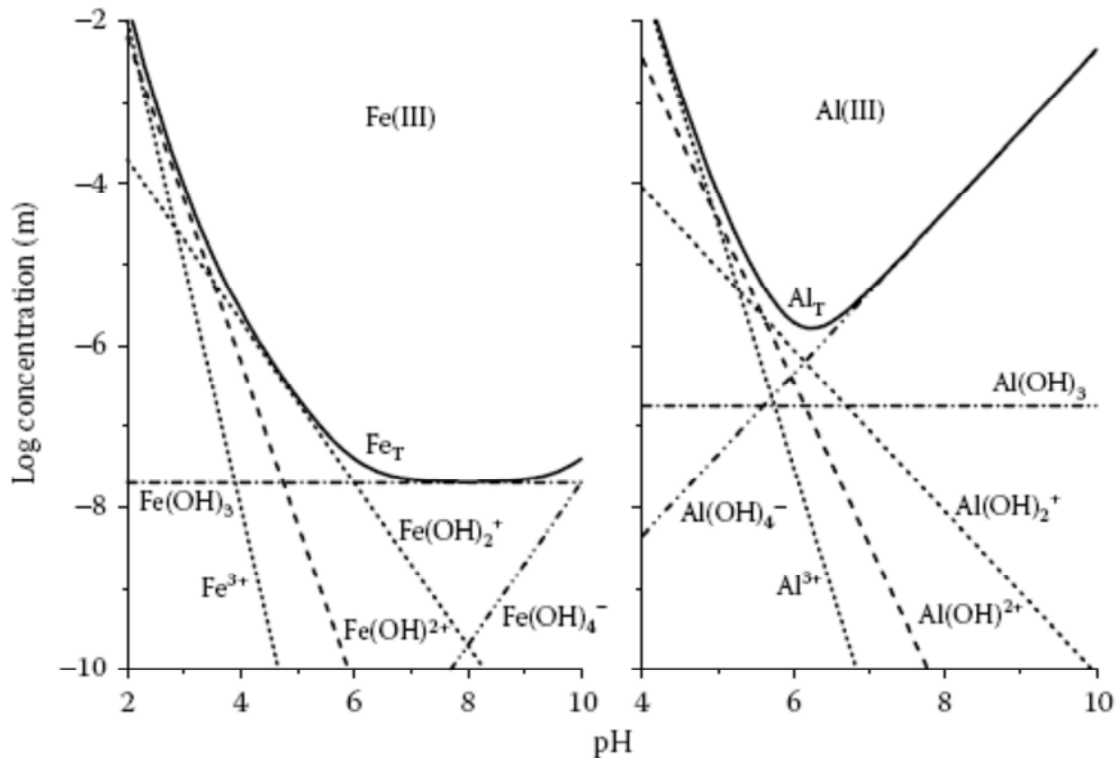


Figure 17. Speciation diagrams for Fe (III) and Al (III) (only monomeric hydrolysis products shown) [40].

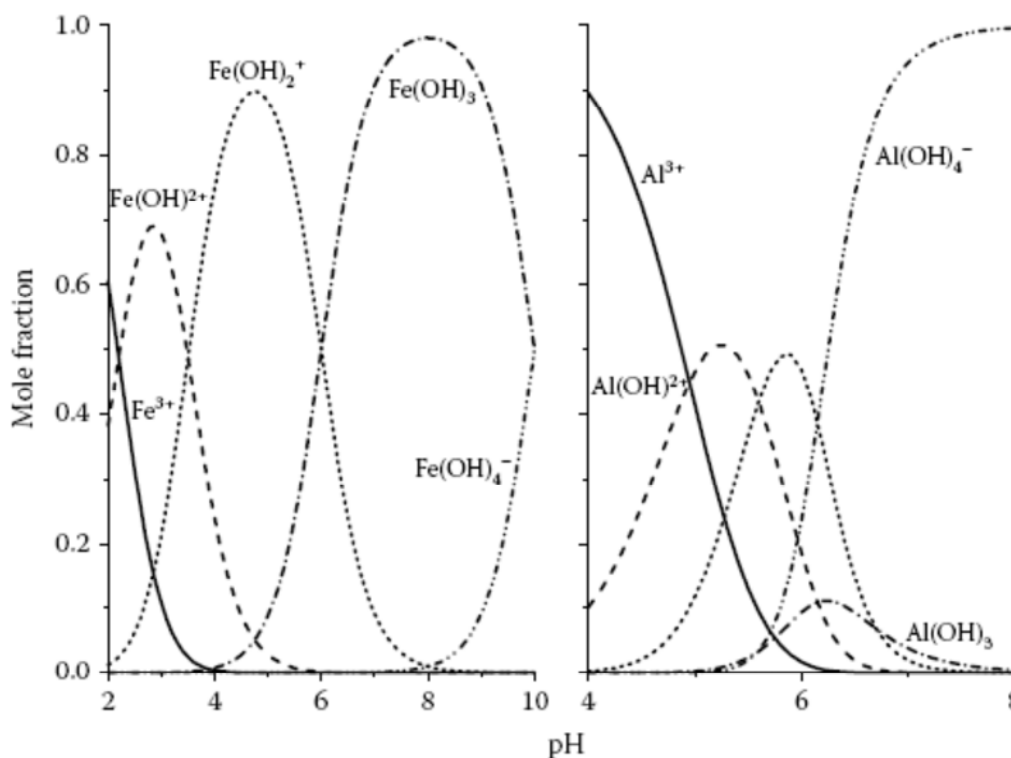


Figure 18. Proportion (mole fraction) of hydrolysed Fe (III) and Al (III) species relative to total soluble metal concentration [40].

Our discussion so far has ignored certain complications, one of which is the effect of various anions that can influence hydrolysis equilibria. For instance, it is known that fluoride forms strong complexes with Al and this gives greater aluminium solubility [58] than would be predicted on the basis of the results in Figure 13. Another point is that only *monomeric* hydrolysis products have been considered, whereas, under some conditions, *polynuclear* species can be important. These form the subject of the next section [40].

6.2.2. Polynuclear Hydrolysis Products

In addition to the monomeric hydrolysis products considered earlier, there are many possible *polynuclear* forms that may be important. For Al these include $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}_3(\text{OH})_4^{5+}$, and there are similar forms for Fe (III). However, these are not likely to be significant at the low concentrations of the metals usually used in coagulation [11, 12]. In practice, only the monomeric forms and the hydroxide precipitate are likely to be important. Polynuclear hydrolysis products can be prepared under certain conditions. The best known of these is $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ or “ Al_{13} ,” which can be formed by controlled neutralisation of aluminium salt solutions or by several other methods [58]. This tridecamer has the so-called keggin structure, consisting of a central tetrahedral AlO_4^{5-} unit surrounded by 12 Al octahedra with shared edges. The tetrahedral and octahedral Al sites can be easily distinguished in the ^{27}Al NMR spectrum. Under appropriate conditions, Al_{13} forms fairly rapidly and essentially irreversibly, remaining stable in aqueous solutions for long periods. The tridecamer is believed to be present fairly widely in the natural aquatic environment, such as in acid forest soil water. Other polynuclear species, such as the octamer, $\text{Al}_8(\text{OH})_{20}^{4+}$, have

been proposed, based on coagulation data [11, 12]. However, there is no direct evidence for the octamer and it is unlikely to be significant in practice. There are many commercial products based on prehydrolysed metal salts. In the case of aluminium [58], a common example is the class of materials known as *polyaluminium chloride* (PACl), which can be produced by controlled neutralisation of aluminium chloride solutions. It is likely that many of these products contain substantial amounts of the tridecamer Al_{13} . In the case of aluminium sulphate [59] it is difficult to prepare prehydrolysed forms with high degrees of neutralisation because sulphate [59] encourages hydroxide precipitation. The presence of small amounts of dissolved silica can significantly improve the stability, and the resulting product is known as *polyaluminosilicate-sulphate*. There are corresponding products containing polymerised iron species, although these are not as widely used as PACl [3, 40, 58, 60-65].

6.2.3. Action of Hydrolysing Coagulants

There are essentially two important ways in which hydrolysing coagulants can act to destabilise and coagulate negatively charged colloids. At low concentrations and under suitable pH conditions, cationic hydrolysis products can adsorb and neutralise the particle charge, hence causing destabilisation and coagulation [11]. At higher doses of coagulant hydroxide precipitation occurs and this plays a very important role — giving the so-called *sweep* coagulation or *sweep flocculation* [11, 12, 40].

6.2.4. Charge Neutralisation by Adsorbed Species

At very low concentrations of metal, only soluble species are

present — the hydrated metal ion and various hydrolysed species (see Figure 17). It is generally thought that hydrolysed cationic species such as $\text{Al}(\text{OH})^{2+}$ are more strongly adsorbed on negative surfaces than the free metal ion and so can effectively neutralise surface charge. Generally, charge neutralisation with aluminium salts occurs at low metal concentrations, usually of the order of a few micromoles/L at around neutral pH. It has been found that, for several inorganic suspensions at pH 6, the amount of Al needed to neutralise the surface charge is around 5 $\mu\text{moles per m}^2$ of particle surface (of the order of 130 $\mu\text{g Al per m}^2$). However, even at very low metal concentrations, the solubility of the amorphous hydroxide may be exceeded. Also, in the region of neutral pH, cationic hydrolysis products represent only a small fraction of the total soluble metal, especially for Al (Figure 18). The fact that charge neutralisation is commonly observed in such cases suggests that the effective species might be colloidal hydroxide particles. In the case of aluminium hydroxide, the point of zero charge, is around pH 8, so the precipitate particles should be positively charged at lower pH values. For ferric hydroxide the point of zero charge is somewhat lower, around pH 7. Even when the bulk solubility is not exceeded, it is possible that some form of *surface precipitation* may occur as a result of nucleation at the surface. Actually, it is difficult to distinguish between surface precipitation and the attachment of colloidal hydroxide particles that have been precipitated in solution. A combination of these effects may be most likely in practice and forms the basis of the *precipitation charge neutralisation* (PCN) model, which is illustrated schematically in Figure 19. Whatever the precise nature of the charge-neutralising species, they are likely to be capable of charge reversal at higher dosages. This means that there will be a characteristic *optimum dosage* at which coagulation is most effective [11, 12]. At higher dosages, particles become positively charged and *restabilised*. The optimum dosage must depend on the particle concentration, but in practice the value is often low. Sometimes, the optimum dosage range can be narrow, so precise dosing control is necessary. Another disadvantage of relying on charge neutralisation is that, for low particle concentrations, the collision rate and hence the aggregation rate will be low, and long times may be needed to give sufficiently large aggregates (flocs). Neutralising surface charge by small adsorbed species does nothing to enhance the collision rate, although, of course, the collision *efficiency* can be greatly enhanced [40].

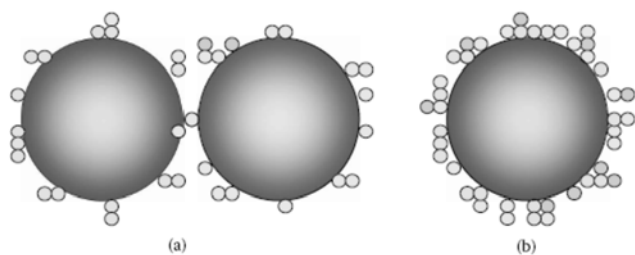


Figure 19. Precipitation charge neutralisation (PCN) model, showing (a) charge neutralisation and (b) charge reversal (restabilisation) of particles by precipitated hydroxide colloids [40].

Some of the advantages claimed for prehydrolysed coagulants are supposed to be a result of the presence of highly charged cationic species, such as $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$. The fact that this ion carries 7 positive charges suggests that it would be very strongly adsorbed on negative surfaces and would be effective in neutralising particle charge (it should be noted that the Al_{13} species has only about half an elementary charge per Al atom, whereas forms such as Al^{3+} and $\text{Al}(\text{OH})^{2+}$ can, in principle, deliver more charge per Al.) Accepting that species such as Al_{13} can be more effective in neutralising charge, it is still difficult to see how, at the optimum dosage, the coagulation rate could be significantly higher than with other adsorbing cationic species [11, 12, 40].

6.2.5. “Sweep” Flocculation

In most practical water treatment operations [2, 3, 15, 43], metal coagulants are added at dosages much higher than the solubility of the amorphous hydroxide and extensive precipitation occurs. For reasons that are still not fully understood, this can give much more effective separation than simple charge neutralisation. The most likely explanation is that the original impurity particles are somehow incorporated into the growing hydroxide precipitate and are thereby removed from suspension. This enmeshment of particles is generally thought of as a “sweeping” action — hence the terms “sweep coagulation” or “sweep flocculation” [11]. The hydroxide precipitate could be regarded as “bridging” particles together and hence “sweep flocculation” might be the more appropriate term from one point of view. Also, in water treatment [2, 3, 15], the formation of large hydroxide aggregates requires some form of agitation, so that orthokinetic collisions are important, and this again supports the use of the term “flocculation.” However “sweep coagulation” is also widely used and it might be better to regard these terms as interchangeable. The aggregates formed as a result of hydroxide precipitation are almost universally known as “flocs.” It is confusing that the additives used are mostly known as “coagulants” [11, 40, 66].

Sweep flocculation almost always leads to faster aggregation than charge neutralisation and gives stronger and larger flocs. The reason for the higher aggregation rate is not hard to find. The production of a hydroxide precipitate gives a big increase in the effective particle concentration and hence a greater collision rate, according to Smoluchowski theory. Hydroxide precipitates are formed from large numbers of colloidal particles, which form very soon after dosing. The aggregation of these small particles gives low-density flocs, with a relatively large volume. According to the theory of orthokinetic aggregation, the rate is directly proportional to the volume fraction of suspended particles, and this can be vastly increased by hydroxide precipitation. This is the main reason why *sweep* flocculation is so much more effective than charge neutralisation. The flocs produced under “sweep” conditions are also stronger and therefore grow larger for the same shear conditions. A major advantage of *sweep* flocculation is that it does not much depend on the nature of the impurity particles to be removed, whether bacteria, clays,

oxides, or others. For relatively dilute suspensions, the optimum coagulant dosage is that which gives the most rapid hydroxide precipitation and is practically independent of the nature and concentration of suspended particles. The large volume associated with hydroxide flocs leads to a significant practical problem — the production of large amounts of sludge that needs to be disposed of in some way. In a typical water treatment plant [2, 3, 15] most of the sludge produced is associated with metal hydroxide rather than the impurities removed from water. Although there is usually no significant restabilisation in the case of *sweep* flocculation and hence no sharp optimum dosage region, overdosing is best avoided to restrict the volume of sludge produced [40, 66, 67].

The action of prehydrolysed coagulants, such as PACl, at typical dosages also very likely involves hydroxide precipitation and *sweep* flocculation, although this point has not been thoroughly investigated. There is evidence that the nature of the precipitate differs from that formed with “alum” [40, 67].

6.2.6. Overview

With increasing dosage of hydrolysing coagulant to a suspension of negatively charged particles, four distinct zones are recognised:

Zone 1: Very low dosage; particles still negative and hence stable,

Zone 2: Dosage sufficient to give charge neutralisation and hence coagulation [12],

Zone 3: Higher dosage giving charge reversal and restabilisation,

Zone 4: Still higher dosage giving hydroxide precipitation and *sweep* flocculation [11, 40, 67].

Figure 20 shows the results of a standard *jar test* procedure, usually used in water treatment applications [2, 3, 15]. In this procedure, a suspension is dosed with different amounts of coagulant under standard mixing and sedimentation conditions. Usually there is a brief *rapid mix* period immediately after dosing. This is followed by a longer period of *slow stirring* during which flocs may be formed as a result of orthokinetic aggregation. These flocs are then allowed to settle for a standard period, after which a sample of the supernatant water is taken and its turbidity is measured. This *residual turbidity* gives a good indication of the degree of removal during sedimentation and hence of the effectiveness of the coagulation/flocculation process [11, 12]. Figure 20 shows that, at very low coagulant dose, the residual turbidity is high, indicating little or no sedimentation (*Zone 1*). As the dose is increased, there is a fairly narrow range (*Zone 2*) where there is a significant reduction in residual turbidity. This is the region of charge neutralisation by adsorbed species, and it is very often found that the particle charge (as measured, for instance, by electrophoretic mobility or streaming current) is around zero. At higher dosages residual turbidity is again high, indicating restabilisation of the particles as a result of excess adsorption and charge reversal (*Zone 3*). Finally, at still higher dosages, there is a substantial reduction in residual turbidity because of hydroxide precipitation and *sweep* flocculation

(*Zone 4*) [67]. Note that the residual turbidity in *Zone 4* is lower than that in *Zone 2*, showing that *sweep* flocculation gives larger, faster-settling flocs than those formed by charge neutralisation [67]. Also, as mentioned earlier, there is no restabilisation after *Zone 4*. The behaviour shown in Figure 20 is typical of aluminium salts at around pH 7. Under these conditions the hydroxide precipitate is positively charged. At pH values near to the isoelectric point (around pH 8) *Zone 2* may not be apparent and only *sweep* flocculation is operative [40, 67].

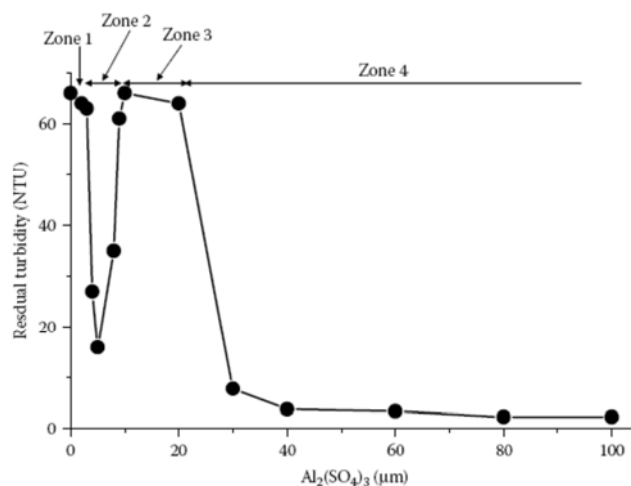


Figure 20. Residual turbidity of kaolin suspensions after coagulation with aluminium sulphate over a range of concentrations at pH 7 [40].

6.2.7. Practical Aspects

There are several important factors that can greatly affect the performance of hydrolysing coagulants. These include the effects of various anions and the influence of temperature. Several common anions can form complexes with aluminium and iron (III) [3, 58, 60-65] and can significantly affect hydroxide precipitation. An important example is sulphate, which is naturally present in water and may be added in the form of aluminium or ferric sulphate in water treatment [2, 15, 66]. Sulphate coordinates moderately strongly with Al, but the main effect is on the precipitation process. On the positive side of the isoelectric point of aluminium hydroxide (i. e., below about pH 8) sulphate can adsorb on the precipitate and reduce its positive charge. This means that the colloidal precipitate can aggregate more rapidly to give large hydroxide flocs [40, 58].

Temperature has effects that are important in practice. In particular, at rather low temperatures, conventional aluminium coagulants tend to perform less well for various reasons. Some prehydrolysed coagulants appear to be less affected by low temperatures and are often preferred for applications in cold regions. Another advantage of prehydrolysed coagulants such as PACl is that, at effective dosages, they produce less sludge than simple metal salts. This may be partly because they can be effective at lower concentrations. Hydroxide flocs, as formed during *sweep* flocculation, tend to be weak and are easily disrupted under high shear conditions. Furthermore, the breakage can be irreversible to some extent so that flocs do not easily reform when the shear rate is reduced [40, 58, 67].

6.3. Flocculation Processes

The main requirements for effective flocculation are as follows:

1. RM of coagulants [68] (Figure 21).
2. Opportunity for collisions of destabilised particles and hence flocculation [40].

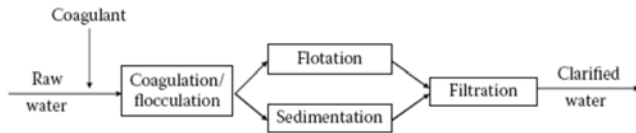


Figure 21. Typical sequence of processes for particle separation in a water treatment plant [40].

For the second step some form of fluid motion has to be generated, which may be by mechanical stirring or flow (or both) [40].

6.3.1. Rapid Mixing (RM)

Mixing is required to supplement coagulant addition to destroy stability in the colloidal system. For particles to agglomerate they must collide, and mixing promotes collision. Brownian movement [10], the random motion imparted to small particles by bombardment by individual water molecules, is always present as a natural mixing force. However, additional mixing energy is almost always required. High intensity mixing, which distributes the coagulant and promotes rapid collisions, is most effective. The frequency and number of particle collisions are also important in coagulation [11, 12]. In low turbidity water, the addition of solids such as clay or the recycle of previously settled solids may be required to increase the number of particle collisions. Essentially RM (sometimes called “flash mixing”) is necessary to distribute the coagulant species among the particles in as short a time as possible [68]. In the case of coagulants that adsorb on particles and neutralise their charge, this can be especially important. Poor mixing can lead to local overdosing of coagulant and hence restabilisation of some particles. For this reason, a short period of intense, turbulent mixing is desirable. The high shear rates associated with RM can also play an important part in the transport of coagulant species and can increase the rate of adsorption [68]. In the case of hydrolysing metal coagulants, under conditions where hydroxide precipitation and *sweep* flocculation [67] are important, the role of RM is not so clear [68]. However, it is known that hydrolysis rates are rapid and it is likely that RM conditions have some role in determining the relative rates of key processes such as adsorption and the formation of precipitates [68]. Ideally, RM needs to be intense but of short duration (no more than a few seconds). Otherwise, the nature of flocs formed subsequently can be affected [68]. Prolonged periods of intense mixing can lead to the growth of small, compact flocs that grow slowly when the shear rate is reduced. RM may be carried out in a flow-through stirred tank (a “backmix” reactor), although this is an inefficient mixing device because of short-circuiting of flow [68]. It is difficult to

achieve complete and homogeneous distribution of added coagulant in a short time (say, less than 1 second). It is more common to add coagulant at a point where there are turbulent conditions as a result of flow. This point may be in a channel — for instance, where water flows over a weir — or in some kind of “in-pipe” mixer. The latter method can involve adding coagulant at a point where the pipe either widens or narrows, as shown schematically in Figure 22 [40].

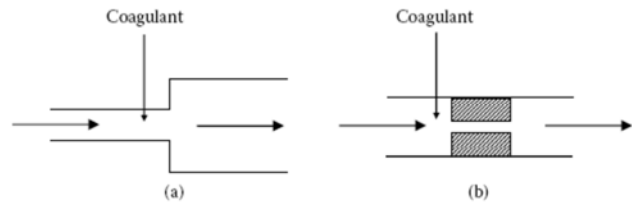


Figure 22. RM of coagulant by “in-pipe” methods [(a) widening pipe; (b) narrowing pipe] [40].

Although RM has long been recognised to have important effects on flocculation processes [53, 54, 68] and has been studied in some detail, it is likely that many instances of poor performance of practical flocculation units can be attributed to inadequate mixing [40, 68].

6.3.2. Floc Formation

In most cases, growth of large flocs requires the application of velocity gradients or shear. The major influences on flocculation rate are the particle (floc) size and concentration and the effective shear rate, G . Higher shear rates give enhanced particle collision rate but may reduce collision efficiency and cause some floc breakage. A useful compromise is a process known as *taper flocculation*, in which the effective shear rate is initially high, giving a rapid flocculation rate, and then progressively reduced so that large flocs can form. In practice, application of shear involves the input of energy. This can be achieved in essentially two ways: *mechanical* or *hydraulic*. Mechanical devices are typified by flow-through stirred tanks of various kinds, sometimes known as *paddle flocculators*. The paddles may rotate about vertical or horizontal axes, but in all cases the power input to the water depends on the drag force on the paddle and the rotation speed. The power input to the water could, in principle, be measured, but it is not too difficult to calculate [40].

6.4. Enhanced Coagulation (EC)

Halogenated organics are formed when natural organic matter (NOM) [12, 17] reacts with free chlorine [69-71] or free bromine [72, 73]. Free chlorine is normally introduced into water directly as a primary or secondary disinfectant [70, 71]. Free bromine results from the oxidation by chlorine of the bromide ion in the source water [70, 71]. Factors affecting the formation of these halogenated disinfection by-products (DBPs) include type and concentration of NOM, chlorine form and dose, time, bromide ion concentration, pH, organic nitrogen concentration, and temperature [53, 69-72, 74-79]. Since most water treatment systems have been required to monitor for total trihalomethans in the past [5, 72, 80], most

water treatment operators are probably familiar with some of the requirements that the Disinfectant/Disinfection By-Product (D/DBP) Rule involve [77]. The key points of the DBP Rule and some of the key changes water supply systems are required to comply with are summarised in literature [53, 72]. However, The D/DBP Rule requires the use of enhanced coagulation (EC) treatment for the reduction of DBP precursors for surface water [14] systems that have sedimentation capabilities [72, 73]. The enhanced process involves modifications to the existing coagulation process such as increasing the coagulant dosage, reducing the pH, or both [11, 12, 17, 18, 53, 70, 72, 73].

Researchers [53] conducted bench, pilot, and demonstration scale studies to examine arsenate removals during EC. The EC conditions in these studies included an increase of alum and ferric chloride coagulant dosage from 10 to 30 mg L⁻¹, a decrease of a pH from 7 to 5.5, or both. Results from these studies indicated the following:

1. More than 90% arsenate removal can be achieved under EC conditions. Arsenate removals above 90% were easily attained under all conditions when ferric chloride was used.

2. EC using ferric salts is more effective for arsenic removal than EC using alum. With an influent arsenic concentration of 5 µg L⁻¹, ferric chloride achieved 96% arsenate removal with a dosage of 10 mg L⁻¹ and no acid addition. When alum was used, 90% arsenate removal could not be achieved without reducing the pH.

3. Lowering pH during EC improved arsenic removal by alum coagulation. With ferric coagulation pH does not have a significant effect between 5.5 and 7.0 [11, 12, 53, 72].

However, post-treatment pH adjustment may be required for corrosion control when the process is operated at a low pH [53, 72].

7. Conclusions

The main conclusions can be summarised as follow:

Entropy can be described as “degree of disorganisation,” that is, the more highly organised a system is, the lower its entropy. Brownian movement, the random motion imparted to small particles by bombardment by individual water molecules, is always present as a natural mixing force. However, additional mixing energy is almost always required. High intensity mixing, which distributes the coagulant and promotes rapid collisions, is most effective. Although RM has long been recognised to have important effects on flocculation processes and has been studied in some detail, it is likely that many instances of poor performance of practical flocculation units can be attributed to inadequate mixing.

Because distinction drawn between coagulation and flocculation, the additives used to cause destabilisation of colloids may be called *coagulants* or *flocculants*, depending on their mode of action. Coagulants would then be inorganic salts, including those containing specifically adsorbing counterions, and flocculants would be long-chain polymers, which give bridging interactions.

After all scientific and technological developments in

coagulation/flocculation field, more much exertion is needed to achieve enhanced control on involved mechanisms – such as the effect of various anions that can influence hydrolysis equilibria – NOM removal and residual metal species in drinking water with particular regard to aluminium, which may induce Alzheimer disease as well as have other carcinogenic properties.

Adding salts simply to increase ionic strength is almost never a practical option and other additives have to be used. However, in seawater where ionic strength is higher due to its *inherent* salts destabilisation processes are easier. Photovoltaically aided distillation process using large basins simulating sea/ocean open sky distillation process would be the *greenest* and healthiest water treatment technology.

Should we assist to a new consideration of coagulation process in terms of energy and entropy? A new revision of coagulation phenomena taking into account the recent advances accomplished in the field of thermodynamics would be envisaged. Thermodynamically, the coagulation process in terms of energy dissipation and rapid mixing, which is followed by slow mixing in the flocculation stage, would be practically better designed.

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