**Evaluation of Flocculation and Filtration Procedures Applied to WSRC Sludge:
A Report from B. Yarar, Colorado School of Mines**

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DISCLAIMER

Westinghouse Savannah River Company (WSRC) contracted with Professor Baki Yarar of the Colorado School of Mines to provide technical support to the Salt Processing Project in the area of flocculation to improve solids liquid separation. The WSRC provided Professor Yarar with a description of the baseline solid-liquid separation process, a description of the feed stream, and test results from the flocculant tests conducted in 2000.[1] In addition, Yarar received sent samples of simulated sludge, monosodium titanate (MST), and effective flocculants.

Professor Yarar reviewed this information and performed tests with the simulated sludge, MST, and flocculants. Following this review, he provided a report that included a general description of flocculation mechanisms, properties of particles in liquids, water-soluble polymer flocculants, optimal conditions for flocculation, the effect of agitation on flocculation, and the effects of system parameters on flocculation. He also provided recommendations for future flocculant tests. Attachment 1 contains the report.

APPROVAL

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[1] M. R. Poirier, "Improving The Filtration Of Sludge/Monosodium Titanate Slurries By The Addition Of Flocculants", WSRC-TR-2001-00175, March 27, 2001.

Attachment 1

Evaluation of Flocculation and Filtration Procedures Applied to WSRC Sludge

Consulting subcontract: AC 18108S

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Evaluation of Flocculation and Filtration Procedures Applied to WSRC Sludge

I. Background

WSRC researchers have been investigating the separation of solids from aqueous slurries as part of their technology development effort. The subject technology relates to the effective removal of radionuclides from processing solutions generated by hydrometallurgical operations in past years.

The solution system contains numerous solids such as iron manganese and magnesium hydroxides arising from past hydrometallurgical work. It also has an unusually-high solution-pH and high ionic strength as can be seen in the following text.

The problem at this stage, is the discovery of optimal conditions for the separation of suspended solids from the aqueous solution. The final stage of the solid-liquid separation process is preferred to be cross-filtration.

This report, addresses fundamentals of flocculation processes shedding light on why WSRC researchers have not been able to report the discovery of a successful flocculant and acceptable filtration rates. It also underscores the importance of applying an optimized flocculation-testing regime, which has not been adopted by these researchers.

The final part of the report proposes a research scheme which should lead to a successful choice of flocculants, filtration aids (surfactants) and a filtration regime, as well recommendations for work that should be carried out to make up for the deficiencies of the limited WSRC work where a better performance should be the outcome.

The overall theme of the report highlights the fact that together with the search for better-performing flocculation additives, and filtration-enhancing surfactants, the process of implementing flocculant usage needs to be based on
   (a) our understanding of the nature of the slurry and
   (b) using a more systematic protocol for the practice of flocculant testing.

A typical approach at WSRC, has been to conduct batch tests that consist of the following steps:

(1) Prepare slurry $\Rightarrow$ (2) Add flocculating reagent $\Rightarrow$ (3) Agitate $\Rightarrow$ (4) Filter

(1) Slurry composition

The slurry is reported to have composition given in Table-1.

Table-1: Composition of the test slurry used by WSC researchers. pH is calculated using $|OH^-| = 1.91$ M and considering the buffering effects of ions such as carbonate, silicate, oxalate and phosphate; ionic strength I is calculated using equation (5) given in the body of the text [1].

Anions	NO_3^-	OH^-	NO_2^-	AlO_2^-	F^-	Cl^-
mol/L	2.14	1.91	0.52	0.31	0.032	0.025
Anions	CO_3^{2-}	SO_4^{2-}	PO_4^{3-}	$C_2O_4^{2-}$	SiO_3^{2-}	MoO_4^{2-}
mol/L	0.16	0.15	0.01	0.008	0.004	0.0002
Cations	Na^+	K^+	Cs^+	pH >12		
mol/L	5.6	0.015	0.00014			
Solids	Sludge	SNT	MST	$I \approx 5.9$		
g/L	0.60	0.55	0.55			

(2) : The reagents used in tests reported are flocculants and filtration aids or surfactants which include the following [2].

   a) Flocculants : Alclar-W 23 ; Superfloc: HX-200, 300, 400, 600, 2000, Magnafloc 336 and hydroxamate-based flocculants all of which are based on polyacrylamide and
   b) Surfactants : Surfynol 110D and 110L, which are fluorinated alky-chain amphipatic substances.

(3) :The agitation process is carried out in 600 mL beakers using a laboratory magnetic stirrer.

(4) : Filtration is carried out using a bench-scale filtration assembly, and filtration rates are recorded as mL/min, for the evaluation of improvement of filtration rate or lack thereof.

As a result of this approach, it is discovered that most of the reagents used, at one test-dosage step, exhibited no significant effect such as raising the filtration rate, except Alclar and hydroxamated reagents which have shown 2-4 times improvement in filtration rates. The results are not surprising since a proper agitation/sedimentation regime has not been applied.

This report is a review-in-context, of the system under study and an attempt to explain the likely mechanisms of action of the reagents used, meaning of the filtration data obtained, and suggestions for future test-work that might improve the sedimentation – filtration process sought.

The problem here, is approached as a solid-liquid separation process that is principally, dominated by the following system parameters:
1) Properties of particles in contact with the solution (dispersed and suspended)
2) Properties of the solution
3) Properties of additives such as flocculants and surfactants, and
4) Solid/liquid/flocculant interactions.

II. Properties of particles in contact with the solution

When insoluble solid particles (called lyophobic particles, in colloid science) are contacted with water, as is the case of the WSRC slurry components under consideration, at least the following simultaneous processes occur in short times:
1) Hydration of lattice ions, isopmorphously substituted elements and non-ionizable sites
2) Release of anions and cations into the aqueous medium
3) Hydrolysis and modification of ions in the medium
4) Adsorptions and re-adsorptions of ions, back on to the lattice and
1) Establishment of an "electrical double-layer" at the solid/liquid interfacial region. The electrical double layer consists of layer-1 which comprises the lattice and strongly adsorbed ions plus layer-2, which is known as the diffuse part of the electrical double layer, comprising the rest of the aqueous medium. Layers 1 and 2 electrically counter (balance) one-another such that at equilibrium, the summation of (+) ve and (-) ve charges in the total system add up to zero, as dictated by the "electro-neutrality principle", $[(\sigma_+ + \sigma_-) = 0]$.
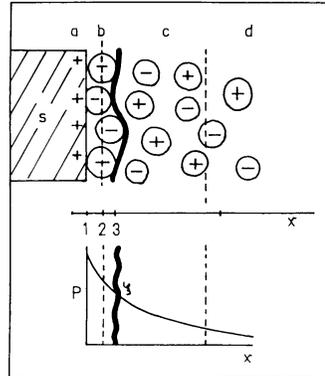
The electrical double layer is schematically shown in Figure-1

The electrical double layer, to a first approximation, can be considered like a plate-capacitor where the solid wall carries an excess charge, likely, negative in the WSRC system due to high pH, and the rest of the solution which adds up to a countering net negative charge. The potential distribution around a suspended particle is shown in the lower part of Figure-1.

Figure 1: Electrical double layer around a suspended particle and the position of the zeta potential (schematic). s: solid; a: lattice ions; b: first adsorbed layer; c: diffuse part of the electrical double layer; d: bulk of the solution; P: potential; x: distance from the wall into the bulk of the solution; z : zeta potential at the shearing surface; heavy line: shearing surface. Electrical layer-1: (a+b); Electrical layer-2: (c+d)

Since potential (in volts) is work done to move charges around, then, the wall of the particle (lattice) and the solution will exhibit a measurable potential, (ζ)

Two identical particles will repel one-another and remain suspended as long as the double layers repel one another. This occurs when their zeta-potentials are $|\zeta > 30 \text{ mV}|$ each.

III. Settling Behavior of Particles

The charged particles in a suspension or dispersion behave in one of two ways:
1) They may settle by gravity, or
2) They may remain suspended until the solid-liquid-particle system is disturbed by alterations of its chemistry or electrical properties.

Settling by gravity

This process will follow Stokes' Law (with its boundary conditions for particle shape, particle concentration, Reynolds number). Spherical particles under conditions of unhindered settling by gravity obey "Stokes' Law" (see eqn. 1) where the variables are viscosity, density, and diameter. Sizes down to 0.1 µm in cases of dense particles can be effected by gravity. However, in most cases Brownian movement is operative at sizes of about $r < 0.5$ µm keeping particles from further sedimentation. Interfacial areas of dispersed particles are determined by their shapes and diameters; with particles of regular geometry, the surface area varies by shape. Thus, the so-called "colloidal size" is determined by the value of the linear-dimension at which interfacial effects, particularly inter-particle repulsions, become significant, rather than by diameter alone.

When particles can sediment in practical time periods by gravity alone, they are described as "particles within the Stokes size range." Thus according to equation-1 below a spherical silica particle ($\rho_s = 2.65 \text{ g/cm}^3$) with a diameter of 0.1 µm would sediment at a velocity of 0.003 cm/hour while a 10 µm diameter would allow the sedimentation velocity to be 32 cm/hour.

$$v = 2 \left[(\rho_s - \rho_l) \, r^2 \, g \right] / 9 \, \eta \qquad\qquad (1)$$

Here
v = velocity of sedimentation (cm/sec)
ρ_s = density of solid (g/cm^3)
ρ_l = density of liquid (g/cm^3)
r = radius of spherical particle (cm)
g = gravitational acceleration constant (cm/sec^2)
η = viscosity of liquid (poise = g/cm.sec); viscosity of water at ambient temperature is about 1 centipoise = 0.01 g/cm.sec

IV. Inter-Particle Forces Operating In Suspensions:

The stabilities of suspensions, that is, whether their solids sediment or not, depend on forces operation among particles. These forces are mainly, of two kinds:

(1) Repulsive inter-particle forces and
(2) Attractive inter-particle forces.

(1) Repulsive forces

Repulsive forces in suspensions arise from two phenomena:
(a) Overlap of electrical double layers carrying the same sign (Coulomb) and
(b) Overlap of lattice fields when particles are so close to one another that overlapping electron-clouds cause repulsions (Born).

(2) Attractive forces

Attractive forces among particles on the other hand, arise from the following effects:

(a) Interaction of oppositely charged double layers (Coulomb)
(b) Interaction of dipoles, induced dipoles and interactions of non-polar atoms (London-van der Waals).

Attractions arising from the non-polar and non-ionizing lattice atoms play an important role in the adsorption of non-ionic flocculants and hydrocarbon oils onto solids. van der Waals attractions operating among non-polar-hydrophobic surface patches create what is know as "hydrophobic bonds".

Each force function among interacting double layers, (attractive = E_A or repulsive = E_R) can be represented by an energy curve and thus, the net interaction energy between particles can be obtained by the summation of these two types of energies as shown, schematically, in Figure 2.
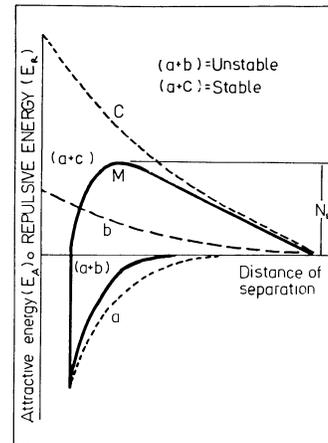

Figure 2: Repulsive energy barrier among two interacting particles in solution [two particles or a particle and a polymeric molecule], (schematic) a: attractive energy; b: repulsive energy at high ionic strength; c: repulsive energy in dilute electrolyte solutions; M: maximum NE ; NE : net repulsive energy barrier which is the summation of energies (a) and (b) or (a) and (c) Note that at NE > 1 kT the particles remain apart and the suspension is stable.

At a certain distance of separation of two particles, depending on the magnitudes of E_A (attractive energy) and E_R (repulsive energy), the net energy of interaction reaches a maximum value (M) which leads to repulsion, if the particles approaching one another have more kinetic energy than N_E (the net energy of interaction).

The suspension is usually stable if the energy barrier (see figure-2) to be overcome is
$(E_R + E_A) \geq 1$ kT.
Here:
k = Boltzmann constant and
T = Absolute temperature.

In the absence of applied agitation, particles acquire their energy from the suspending medium, largely as a function of temperature.

In suspensions containing particles of different sizes, especially if the large particles are 1 µm or larger, the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory of colloid stability [3, 4] permits calculations that a so-called "secondary minimum" should occur for particles larger than 1 µm. The coagulation of such coarse particles could take place despite a relatively high electrostatic repulsions which, in fact, has been confirmed with model particles of 10 µm diameter.

V. Effect of Solids Concentration On Suspension Stability

Increased crowding of particles in a suspension augments the rate of inter-particle collisions and under conditions where each collision leads to permanent contact between particles, the initial rate of coagulation would increase. According to Smoluchowski [5] when the movement of particles is controlled by diffusion and the potential energy barrier to be overcome is negligible (this is the case of the WSRC slurry which has a very high ionic strength), the number of spherical particles remaining after a coagulation time (t) will be:

$$N = (N_o /1 + 4\pi DrN_o t) \qquad (2)$$

Here:
N_o = Initial number of particles,
D = Diffusion coefficient, and
a = Effective radius of particles.

In the presence of a repulsive energy barrier (M) the coagulation is slowed down by a factor (W), and according to an approximate theory due to Fuchs [4] W is given by:

$$W = [(2 K r)^{-1} \exp [M /kT] \qquad (3)$$

Here

(K^{-1}) = Thickness of the electrical double layer and

M = Potential energy maximum on the particle-particle interaction energy curve

T = Absolute temperature and

k = Boltzmann's constant.

"Perikinetic" coagulation processes acquire their energy from Brownian notion only, whereas "orthokinetic" coagulation processes occur under slow agitation. Heterodisperse, that is, containing a wide range of particle sizes, systems exhibit stronger orthokinetic coagulation.

VI. Properties of The Solution

As far as their effects on the surface chemistry of suspended solids is concerned, aqueous solutions have ions that fall into two groups:

(1) Potential determining ions (pdi) and

(2) Indifferent ions.

Potential Determining Ions

Potential determining ions are typically the same as lattice ions (as in Ca^{2+} or CO_3^{2-} of $CaCO_3$) and ions that can adsorb strongly at lattices. Strong adsorptions also known as chemisorptions, are characterized by a bond energy of $E_b \geq 10$ kcal/mol of bonds. H^+ and OH^- are ubiquitous potential determining ions and the WSRC sludges have exceedingly high concentration of the latter.

Indifferent Ions

Indifferent ions remain within the outer (diffuse) part of the electrical double layer, and do not strongly adsorb at the solid wall. Their action is important, in that, they compress the electrical double layer and thus reduce the value of the ζ-potential and reduce the inter-particle repulsions that would otherwise, keep the particles suspended. They act as coagulants or suspension destabilizers.

Thickness of the double layer (K^{-1}) relates to the ionic strength of the solution as follows:

$$K^{-1} = (3/I^{\frac{1}{2}}) \qquad\qquad (4)$$

where

$$I = \frac{1}{2} 3c_i z_i^2 \qquad\qquad (5)$$

Here:

I = Ionic strength of the solution

K^{-1} = Thickness of the electrical double layer (Δ units)

c_i = concentration of any ion (i) (mol/L) and
z_i = valency of this ion (an integer).

VII. Zeta-potential

The zeta-potential of a particle represents the value of potential at the shear surface of the solid/liquid interfacial region when fine particles are made to move in an externally-applied electric field under a constant potential drop and is given for electrophoresis by equation 6.

$$\zeta = 4 \pi \eta \ V_e / \ \varepsilon E \qquad (6)$$

where:
ζ : zeta potential (mV)
η : viscosity of the medium (poise)
ε : dielectric constant of the medium
V_e: velocity of motion and (μm/sec)
E : potential drop between electrodes (V/cm)

In practice, the ζ-potential is determined by various techniques including micro electrophoresis, electro-osmosis, sedimentation potential or streaming potential.
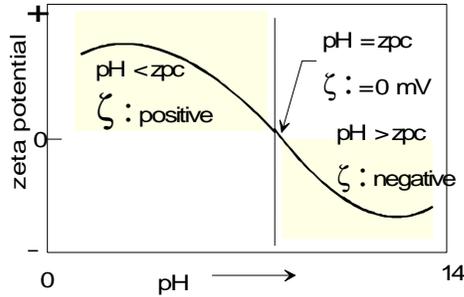

Figure 3: Relationship of zeta potential and zero point of charge.

A value of the order of $\zeta = \pm 30$ mV is usually observed as the limit for the stability of such dispersions and when $\zeta > \pm 30$ mV the suspension is stable and at $\zeta < \pm 30$ mV slow coagulation sets in [6].

In this context, the zero point of charge, zpc, indicates the concentration of ions where $\zeta = 0$ mV. As can be seen from Figure-3, for a given particle, at pH < zpc the zeta potential is positive and at pH > zpc it is negative. The pH values at which the zpc of some solids (relevant to WSRC slurries) occur, are given in Table-2.

Table-2 Zero point of charge values of some of the solids, (pH).

Solid	SiO_2	TiO_2	Fe_2O_3	$BaSO_4$	$Ca_3(PO_4)_2$	$CaCO_3$	Al_2O_3	MgO
zpc (pH)	2-3	5.9	6.7-8.5	9.7	6.4-8.5	10.8	9.1	12.4

The zeta-potentials of WSRC solids can not be measured due to two reasons:
1) High ionic strength causing $\zeta \cong 0$ and
2) High electrolyte conductivity.

VIII. Aggregation, Coagulation, and Flocculation

Particles with high zeta-potential values will remain suspended, as long as they are small-enough to be outside of the Stokes-size-range and keep repelling one another by virtue of overlap of their electrical double-layers. Parameters that affect inter-particle interactions define whether the colliding particles will stay together, forming a permanent aggregate, "coagulum", or bounce apart.

The aggregation of suspended particles under the influence of salts or polymers occurs by two mechanisms:
1) Coagulation and
2) Flocculation

Coagulation

In coagulation, the rates of aggregation and sedimentation are low and the final sediment volume is compact while in flocculation the rates of aggregation and sedimentation are high and the final sediment is voluminous.

The primary characteristics of coagulation are as follows:
  a) Aggregation occurs under the influence of high ionic strength solutions which compress the electrical double layer to such an extent that the particles come close-enough together that they enter the range of effect of van der Waals forces which hold the particles together. van der Waals forces exist in all matter and are always attractive.
  b) Aggregations may occur by the aid of multi-valent salt ions that form a bridge among suspended particles and/or neutralize wall charges
  c) Volume of the sediment is small
  d) Re-agitation of the sediment leads to re-dispersion but the aggregation-sedimentation process resumes as soon as agitation is stopped.
  e) Excessive salt concentrations do not cause re-stabilization of the sedimented particles.

Flocculation

The aggregation process in flocculation is brought about by added polymeric substances. The primary characteristics of the flocculation process are as follows:
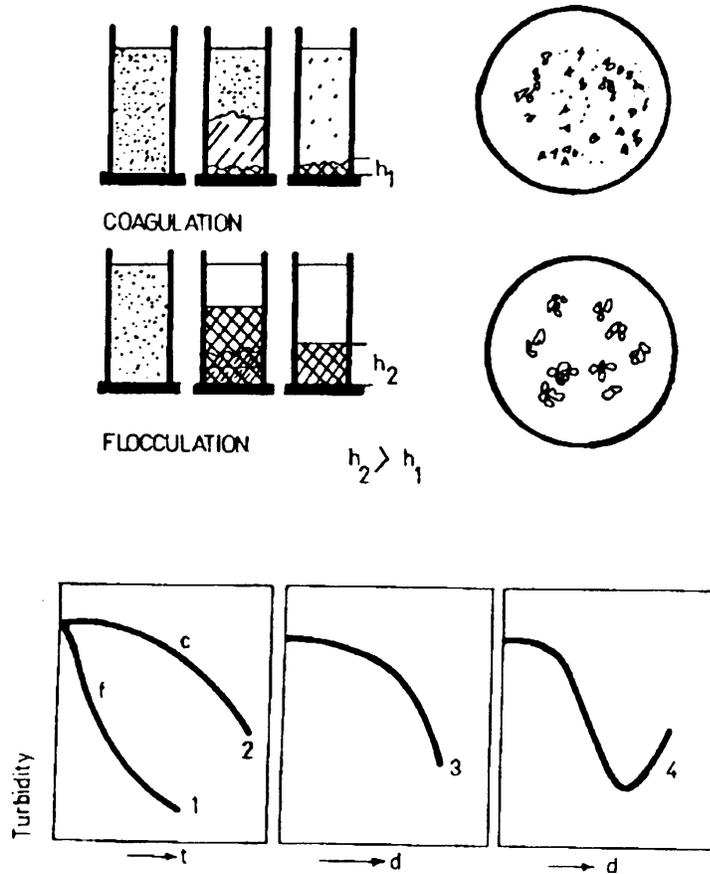
Figure 4: Comparison of coagulation and flocculation processes. f: flocculation; c: coagulation; t: time; d: dose of additive. Compare lines 3 and 4 and note that in coagulation (3) overdosing does not occur while in flocculation (4) an excess concentration of flocculant may lead to the re-stabilization of the suspension resulting with a reversal of supernatant turbidity.

a) Aggregates (flocs) are relatively large (fraction of a millimeter to a few centimeters) and settle at a high rate
b) Volume of the sediment is large
c) Re-agitation of the sediment may or may not lead to re-stabilization of the suspended particles
d) Excessive flocculant concentrations often lead to irreversible re-stabilization

Characteristics of coagulation ad flocculation are schematically summarized in Figure-4

There are three mechanisms of flocculation:

(1) Bridging mechanism
(2) Charged-patch neutralization and
(3) Blanketing by hydrogen-bonded molecular networks.

Bridging mechanism

In the bridging mechanism, the polymeric chains, as the name implies, form bridges among suspended particles, and create flocs which sediment by gravity since at such sizes they are within the size range of Stokes' law.

Figure 5: Polymer bridging mechanism (schematic)

Here, the distance between suspended particles is spanned by a polymeric string, in effect increasing the sizes of suspended entities. See Figure-5.

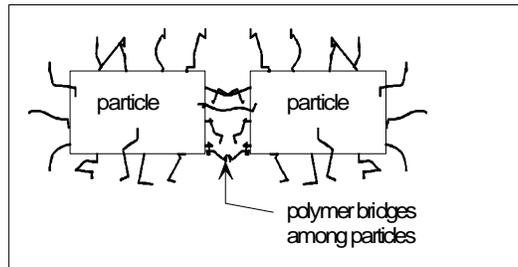This mechanism is supported by extensive experimental evidence.

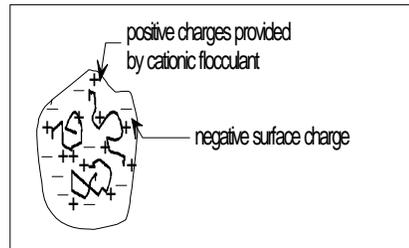Charged-Patch Neutralization

Figure 6: Charged-patch neutralization model of flocculant action (schematic)

Coagulation occurs if suspended particles exhibit a low repulsive energy barrier, and this can be caused by means of added salts. Polymeric flocculant molecules can act, much the same as coagulants, as charge neutralizing units-if their active groups are of opposite sign to that of the net charge sign of the particle, simultaneously acting as bridging agents. This model is illustrated in Figure-6.
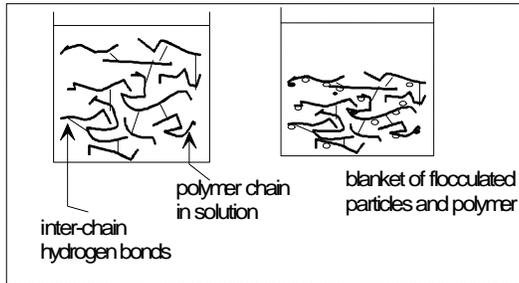
Figure 7: Network (or blanketing) model of flocculation (schematic)

Network Model

In this model which is less commonly recognized, the polymer solution is assumed to form "a network" through hydrogen bonding, inter chain cross links by multivalent ions, London-van der Waals bonds or other available bond formation mechanisms. See Figure-7.

IX. Water-Soluble Polymers as Flocculants

Stable suspensions may be flocculated, by the addition of certain organic polymers of high molecular weight. These are known as "poly-electrolytes" or "water-soluble-polymeric-flocculants". Mixtures of lime and starch, glue and gelatin are also used as flocculants. Water-soluble polymers can be classified according to their sources, their constitutions and/or the ionic properties they exhibit in aqueous media. See Table-3.

According to sources, they are classified as:
 (1) Natural,
 (2) Modified natural and
 (3) Synthetic.

According to their predominating active groups they are classified as:
 (1) Non-ionic,
 (2) Anionic and
 (3) Cationic.

Two more terms are used to describe commercial products:
Homopolymer , indicating a polymer that has only one kind of functional group, as in pure non-ionic polyacrylamide (see Table 5) and
Copolymer , which indicates a polymer that contains both ionic and non-ionic functional groups as in partially hydrolyzed polyacrylamide that contains both anionic and non-ionic functional groups (see Table 6).

Table-3: Classification of flocculants

Source	Type		
	Non-ionic	Anionic	Cationic
Natural	Guar gum Starch(es)	Alginates	-
Modified natural	Dextrin	Causticized starch Carboxy methyl cellulose Lignosulphonates	-
Synthetic	Polyacrylamide Poly ethylene-oxide Poly vinyl alcohol Alkyl hydoxamate	Hydrolyzed polyacrylamide Sodium polyvinyl sulphonate Sodium polystyrene-sulphonate	Polyethylene imine Polyacrylamide Poly vinyl pyridinium bromide

Table-4: Examples of water-soluble, polymeric flocculants. (1): Sodium polystyrene sulfonate, (2): Sodium polyacrylate, (3): Polyvinyl-xanthate, (4): Polyvinyl-pyridinium-bromide, (5): Poly ethylene-imine, (6): Polyethylene-diamine, (7): Quarternary substituted-polyacrylamide, (8): Polyvinyl-alcohol, (9): Polyethylene-oxide, (10): Polyacrylamide

Notably, many of the commercially available flocculants contain more than one type of functional group, and some synthesis by-products in the form of inorganic salts. Emulsified products contain mineral oils added NaOH and NH_3 in high proportions. Currently, it is estimated that more than 500 trade names are marketed and the patent literature abounds with new arrivals. Regretfully, often, the same product is marketed under different trade names by the same manufacturer or its affiliates. Flocculant classes and examples are given in Table-3 and explicit chemical formulas of the primary active ingredients of commercial flocculants are given in Table-4**.**

The chemical structures of synthetic-polymeric flocculants carry two common features:
  1) They consist of a hydrocarbon backbone forming a long chain and
  2) The long chain carries active groups, which can be anions, cations or no-ionic entities.

This common structure is illustrated in Figure 8 for an anionic polyacrylamide molecular segment. The chemistry of common functional groups (active groups) is shown in Tables-5 and 6.
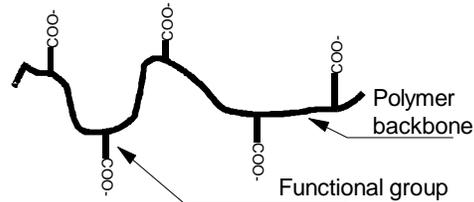
Figure 8: A typical synthetic polymeric flocculant molecule consists of a hydrocarbon back bone and attached functional groups. Here the -COO- indicates an anionic flocculant.

X. Properties of Commercially-Available Flocculants

Commercial synthetic flocculants are offered to the end-user in three forms:
1) Solid powders
2) Liquids and
3) Emulsions

Solid powders and liquids, in water, form viscous polymeric molecule networks.

Emulsions , are usually W/O (water-in-oil) emulsions where water droplets, dispersed in a mineral oil carry the polymeric flocculant as a solution as schematically illustrated in Figure 9.

Table-5 : Typical non-ionic functional groups in commercially-available flocculants

CHEMICAL TYPE	FUNCTIONAL GROUP	TYPICAL EXAMPLE	
Polyalcohols	$-OH$	Polyvinyl Alcohol	$\left[CH_2 - \underset{\underset{OH}{\vert}}{CH} \right]_x$
Polyamides	$\underset{\vert}{\overset{\overset{C}{\parallel}}{-C}} - NH_2$	Polyacrylamide	$\left[CH_2 - \underset{\underset{\underset{NH_2}{\vert}}{\underset{C=O}{\vert}}}{CH} \right]_x$
Polyethers	$-O-$	Polyethylene Oxide	$\left[CH_2 - CH_2 - O \right]_x$

Table-6 : Typical non-ionic functional groups in commercially-available flocculants

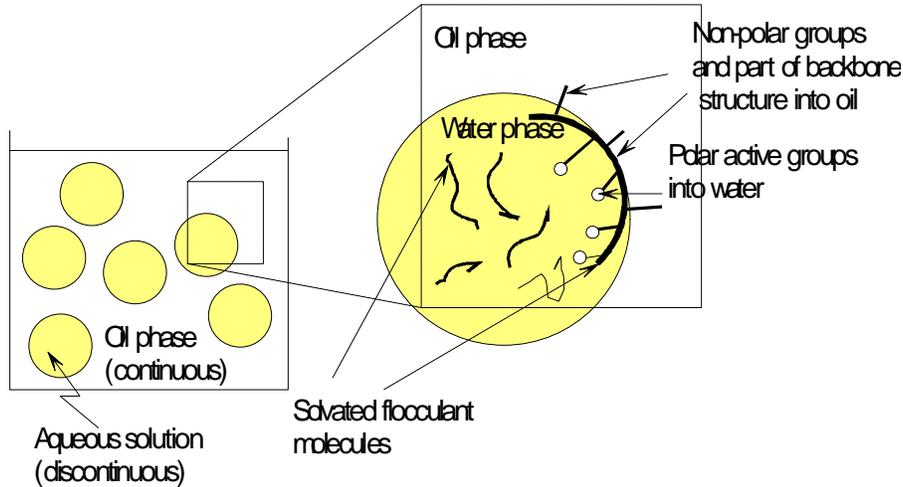| CHEMICAL TYPE	FUNCTIONAL GROUP	TYPICAL EXAMPLE	
Carboxylic	$\overset{\overset{O}{\parallel}}{-C} - O^- H^+$	Polyacrylic Acid	$\left(CH_2 - \underset{\underset{\underset{O^- M^+}{\vert}}{\underset{C=O}{\vert}}}{CH} \right)_x$
Sulfonic	$\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{-S}} - O^- H^+$	Polystrene Sulfonic Acid	$\left(CH_2 - \underset{\underset{\underset{O^- M^+}{\vert}}{\underset{O=S=O}{\vert}}}{CH} \right)_x$
Partially Hydrolyzed Acrylamide	$-CH_2 - \underset{\underset{\underset{NH_2}{\vert}}{\underset{C=O}{\vert}}}{CH} -$ Acrylamide	$\left(CH_2 - \underset{\underset{\underset{NH_2}{\vert}}{\underset{C=O}{\vert}}}{CH} \right)_x \left(CH_2 - \underset{\underset{\underset{O^- M^+}{\vert}}{\underset{C=O}{\vert}}}{CH} \right)_y$ Copolymer of Acrylamide and Acrylic Acid	
	$-CH_2 - \underset{\underset{\underset{O^- M^+}{\vert}}{\underset{C=O}{\vert}}}{CH} -$ Acrylic		

Figure 9: Emulsion-type commercial flocculants. The continuous (dispersing) phase is a mineral oil and the discontinuous (dispersed) phase is an aqueous polymer solution. Emulsion-formation, and emulsion stability are facilitated by added alkalis and ammonia. The flocculant molecules themselves also act as emulsification aids by their orientations at the liquid/liquid interface.

XI. Adsorption and Flocculation

Flocculation needs to be preceded by polymer uptake; however, not all polymer adsorptions produce flocculation. In high-salt-concentration media flocculation is largely hindered, and dilution, which reduces salt concentration, can lead to dramatic results where flocculation resumes. This phenomenon is attributed to the coiling up of flocculant molecules by the high ionic strength, which reduces their effective chain-lengths. Dilution simply reduces the adverse effect of salts. In fact it can be shown by experiment that the viscosity of flocculant solutions is reduced by elevated salt concentrations, which supports the contention that high salt concentrations reduce apparent molecular weights.

Polymer adsorptions occur as a function of solid surface chemistry and the nature of the functional groups of the polymer. The likely adsorption mechanisms are discussed below:

Hydrogen Bonding
Hydrogen bonding occurs when hydrogen is attached to an electronegative element such as O, F, N, or S. The interaction of freshly ground natural silica or clays, with non ionic polyacrylamide has been shown to be by this mechanism.

Electrostatic Interactions
Coulombic, or electrostatic interactions take place if the functional groups of the polymer and the solid wall are oppositely charged. The attraction is non-specific and results with mutual charge neutralization and even charge reversal. The flocculating action of cationic flocculants on solids that carry a zeta-potential with a negative sign is usually of this nature.
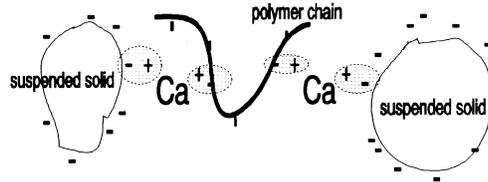

Figure 10: The activator action of a divalent cation such as calcium in facilitating the adsorption of an anionic flocculant on to a negatively charged suspended solid.

Electrostatic Interactions by The Agency of Ion-Bridges
Multi-valent cations may also act as bridges between anionic sites in the polymer chain and particles. The adsorption of polyacrylic acid by silica with the help of multi-valent ions such as Ca^{2+} takes place by this mechanism, as illustrated in Figure-10.

Chemical Interactions
Such interactions are characterized by the fact that the bond resulting from the reaction among polymeric functional groups and the solid wall is strong [$E_b \geq 10$ kcal/mol.] Typically, anionic groups of polyacrylamide adsorb at lattice metal sites by this mechanism.

Crystal field interactions

This mechanism is different form coulombic interactions, in that the electrostatic field created by some crystals can cause the formation of weak bonds among the functional group of polymers and particle walls. The flocculating action of non-ionic polymers on CaF_2 (fluorite mineral) has been attributed to the interaction of the dipoles of the amide group [$-NH_2$] with the electrostatic field of the surface of the ionic crystal.

Hydrophobic Bonding

The bond that forms among hydrophobic entities such as mineral oil droplets and non-water-wettable patches of the solid wall are named "hydrophobic bonds". Bond formation is due to London-van der Waals forces.
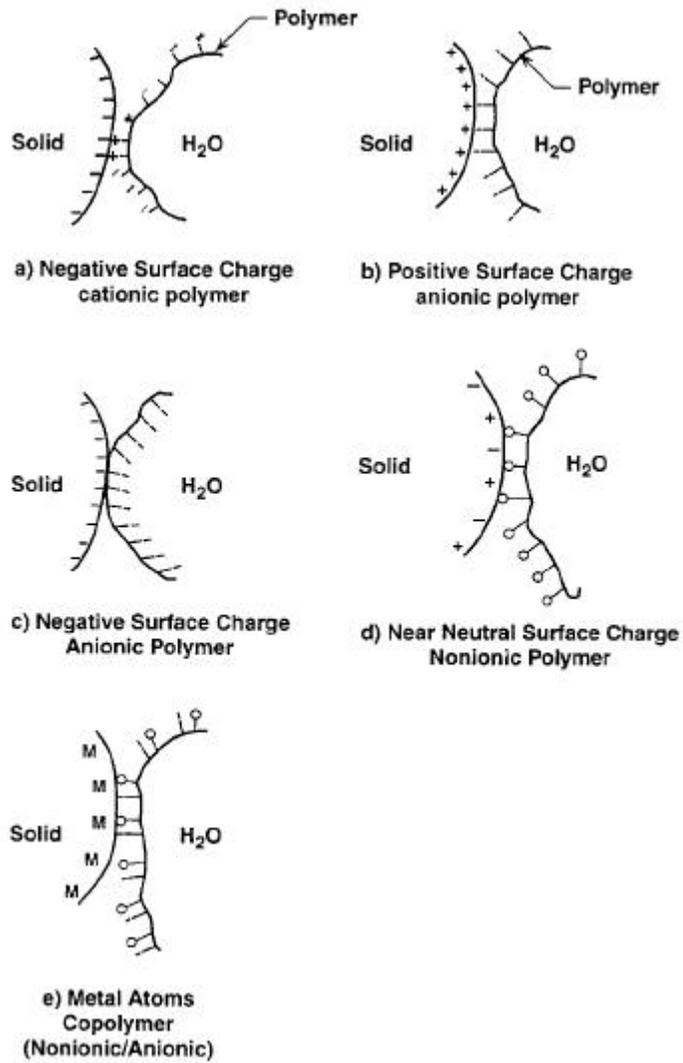
Figure 11: Examples of how flocculants may adsorb at various interfaces as a function of lattice constitution, charging and polymeric functional groups.

Schematic illustrations of common adsorptions of polymers at solid-liquid interfaces are given in Figure 11.

It is evident from the discussion above, that depending on the nature of the interaction energy involved between the solid and the active group of the polymer the nature of the chemical bond involved in adsorption process can be expected to vary. In all cases, however, it is probable that polymers require a large number of points of attachment for strong adsorption. The possible effects of the solvent and temperature will play roles. Incidentally, this aspect of flocculation has not been widely studied.

XII. Optimal Conditions of Flocculation

A typical flocculation process is carried out by adding a few milliliters of flocculant solution to the slurry under agitation and following the progress of solution clarification when agitation is stopped. Following the liquor clarification can be made by numerous methods. Two of these are:
1) following the rate of descent of the boundary between the flocculated mass and the clear supernatant liquid above it and
2) measuring the clarity (light-transmittance) of the clarifying supernatant solution.

The first method is more useful with high-solids-content slurries and the second one is appropriate with dilute slurries.

These methods of monitoring of the flocculation process are known as "flocculation index". While there are many alternatives to them, they serve adequately in most systems and are relatively easy to perform.

Figure 12: Effect of polymer dose (p.p.m. in solution or grams/ton added) on the flocculation-redispersion behavior of a suspension

Using this two-step approach (flocculate under agitation and follow supernate clarity) optimal conditions of flocculation are established by monitoring two variables:

1) Flocculant concentration or "dose" expressed as ppm flocculant, or g/ton of contained solids and
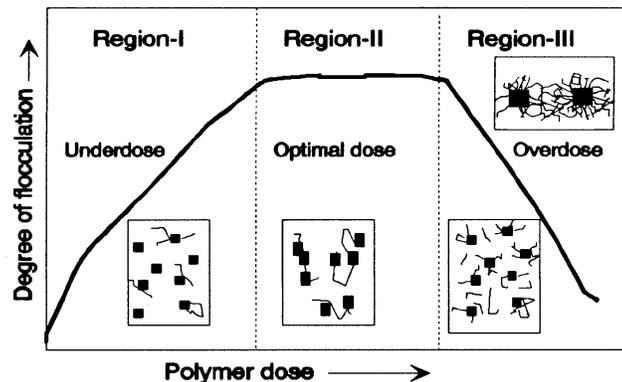2) Agitation regime.

Flocculant Dose

A supernatant-clarity versus flocculant dose curve would look like the one shown in Figure 12. In this figure, in agreement with the bridging mechanism of flocculation, 3 regions can be observed:
- i) Underdose region
- ii) Optimal dose region and
- iii) Overdose region.

Underdose region
In this case there is not a sufficient number of polymer chains to bind all of the particles into flocs.

Optimal dose region
Under these conditions the number of polymeric chains is sufficient for optimal flocculation. Optimum flocculation occurs when only part of the available adsorption sites are occupied by the active functional groups of the polymer. When solid particles are half covered by polymer, optimum flocculation can take place.

Overdose region
In this case, there are more polymeric chain molecules than needed to cause flocculation. The excess molecules wrap around the particles making them behave as if they were beads of polymer. Such particles repel one another and remain suspended.
The polymer chain is initially adsorbed through a few active groups on the particle, the rest of the molecule extending into the solution and eventually adsorbing onto another particle upon colliding with it. Failing this, the polymer adsorbs on other available sites of the original particle thus reducing the possibility of polymer bridging.

XIII. Rate of Shear (agitation regime)

The agitation process, during flocculant addition is an important step that determines the success or failure of the operation. The guiding principle here is based on two steps of operation:

- 1) Addition of flocculant solution at high rate of shear
- 2) Followed by a slow agitation step

The high-shear step ensures that the flocculant molecules are homogenously distributed in the slurry while the subsequent low-shear step allows the small flocs to collide, yet not break and thus grow to their hydrodynamically-stable final sizes.

Under too low or too high an intensity of agitation only partial flocculation takes place because of inhomogeneous distribution of flocculant. At high shear, flocs break apart. This breakage occurs at the polymer-particle bonds and not at the -C-C- bond of the polymer chain, owing to the relative bond strengths involved.

The effect of agitation regime on the clarification of $CaCO_3$ suspensions by an anionic flocculant is illustrated in Figure 13. In this figure, it can be observed that better clarification is obtained if the flocculant is added under high intensity agitation followed by a slow step of conditioning (curve B), giving particles time to collide less-vigorously, and thus retain the solid-polymer bridges as they grow.

Evidently, the intensity of each agitation step will depend on the size and shape of the agitation vessel and the configuration of the agitation paddle, whether turbine or baffle etc.

XIV. Effects of Molecular Weight and other system parameters

The bridging mechanism indicates that increased molecular weight of a polymer should increase the efficiency of flocculation, since a longer chain should bridge more effectively. Numerous investigators have reported evidence supporting this hypothesis. Kuzkin and Nebera [7], for example, have calculated for a series of polyacrylamide based flocculants an end to end length of up to 10^4Å. Spetch [8], calculated a similar end to end

Figure 13: Effect of agitation regime on the flocculation of a $CaCO_3$ powder suspension with anionic polyacrylamide at constant dose. A: no slow conditioning step, stirring time: 2 min.;   B: flocculant solution flows at indicated rpm followed by 400 rpm (times: 1 min. + 1 min.); C: reagent flows at 2100 rpm followed by indicated rpm as conditioning speed. (times: 1 min. + 1 min.) [9]

length for a stretched chain of 1 million molecular weight. The above notwithstanding, lower molecular weight polymers (i.e., M.W. < 1 million) can also bridge particles provided that the surface charge is low enough for a close approach of the particles, or if the adsorbed polymer reduces the potential by charge neutralization, thus reducing inter-particle repulsion. This is the likely scenario with the WSRC slurries as well.
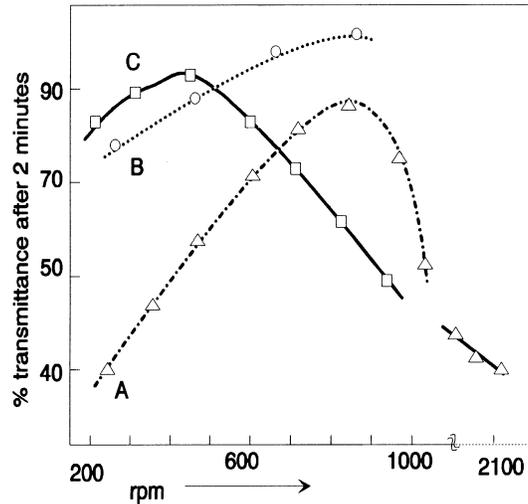
Table-7 : Variables of Flocculation Systems and Their Effects on Optimization Tests

Property	Likely Observations and Effects
Molecular weight increase	Poorer solubility Higher viscosity solutions Chains more shear sensitive Higher unit cost Higher optimal dose Bridging favored Larger flocs Higher sediment volume Higher water retention Faster settling
Dose increase	Better flocculation up to optimal
Shear increase	Break down of long chains Irreversible floc degradation Smaller equilibrium size flocs
Particle surface area increase	Increased flocculant consumption Ultra fines susceptible to overdosing and re stabilization
Particle concentration increase	Does not always affect optimal dose, Smaller or perhaps longer flocs, local overdosing possible

Suspension pH	Non-ionics little affected
	Ionization and extension of anionics at
	  alkaline pH-converse of cationics, also
	  alters particle charge, combined effects
	  on flocculants is complex.

Suspension ionic strength	Similar comments as for suspension pH-Can promote flocculation or inhibit. Excess salt lowers solubility and coils polymer.

Polymer charge density increase	Extends polymer in solution under suitable
	  conditions, decreases adsorption onto
	  particle of similar sign.

Commercially available polymeric flocculants contain a range of molecular weights and in suspensions, the lower molecular weights might be expected to adsorb more rapidly as they can faster diffuse to the surface. It appears from available evidence that although preferential adsorption of low molecular weight chains may take place, if adsorption is irreversible the high molecular weight chains are not adsorbed; if it is reversible however, then the high molecular weight chains do eventually displace the smaller adsorbed ones.

As was noted earlier in this text, solids content, pH, salt content, nature of the salt-forming ions, and nature of the flocculants, as well as the nature of nature of the solids contained have their combined contributions to the outcome of the flocculation process. A summary of these parameters is compiled in Table-7.

XV. The WSRC Slurry

The following is a discussion of the properties of the WSRC slurry and how these properties affect the flocculation behavior of its solid constituents.

The significant properties of the WSRC slurry with reference to the flocculation of suspended matter can be outlined as follows:

1) The suspending medium has an exceedingly high ionic strength
2) The pH of the medium is unusually high $[OH^-] = 1.91$ M $\Rightarrow$ pH = 13.7 modified to a slightly lower value by the presence of buffering ions.
3) The medium has hydrolysable cations such as Al^{3+}, which is in the hydrolyzed form $Al(OH)_4^-$ (or AlO_2^-)

1) <u>Ionic composition of the slurry</u>
The ionic composition of the slurry is shown in Table 1 of this report where it is seen that the ionic strength is I = 5.9 and solution pH is, pH > 12.

2) <u>Electrical double-layer and ζ-potential</u>
In such high ionic strength media no significant electrical double layer should be expected. Using equation 4 the thickness of the electrical double layer comes out to be
$K^{-1} = 1.2$ X
This value indicates that the electrical double-layer is virtually non-existent beyond 1 or 2 atomic layers. The zeta-potential of particles that carry such a small K^{-1} so small, will be essentially un-measurable, thus:
$\zeta = 0$ mV

3) <u>Effect of high pH on flocculant molecules</u>

a) Effect on ionization properties

High pH renders cationic flocculants less ionic

$[-CH_2-(CH-C=O)-NH_3\ ]_x^+ + OH^- \Rightarrow [-CH_2-(CH-C=O)NH_2\ ]_x + H_2O$
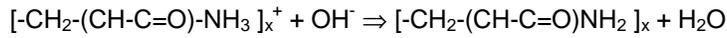
High pH increases the anionic character of carboxylic acid-based active groups of anionic flocculants (as in polyacrylamides or hydroxamated polyacrylamides)
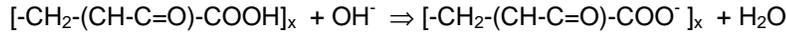
$[-CH_2-(CH-C=O)-COOH]_x + OH^- \Rightarrow [-CH_2-(CH-C=O)-COO^-\ ]_x + H_2O$

Table 8 : Summary of the ionization properties of typical functional groups of polymeric flocculants

Active group	Name	Ionization properties
$-(C=O)-O^-$	Carboxyl	Ionized at pH >10, becomes $-(C=O)$-OH at low pH
$-(C=O)NH-O^-$	Hydroxamate	Similar to carboxyl
$-NH_3^+$	Amine	Ionic at low pH, becomes $-NH_2$ at high pH
$-NH_2$	Amide	Non-ionic at low or high pH
$-O-$	Ether	Non-ionic at low or high pH
$-OH$	Alcohol	Non-ionic at low or high pH

High pH, especially at prolonged contact times or elevated temperatures, can hydrolyze the non-ionic active groups of polyacrylamide, converting the flocculant, to partly or completely anionic.
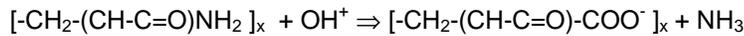
$[-CH_2-(CH-C=O)NH_2\ ]_x + OH^+ \Rightarrow [-CH_2-(CH-C=O)-COO^-\ ]_x + NH_3$
The ionization properties of these functional groups are summarized in Table 8.

4) Effect of high ionic strength on flocculant molecules

The apparent molecular weights of all polymers will be reduced due to coiling as shown in Figure 14 parts (A) and (B). Coiling, reduces the effective molecular weight and ability to bridge long distances among particles. The high ionic strength medium will also create an organized crowd of anions and cations that constitute a screening cloud around the functional group as shown in Figure 14 (C).
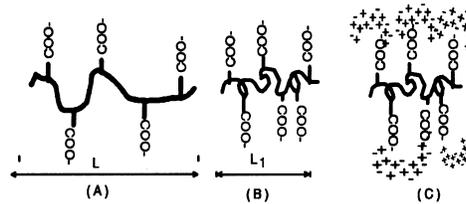

Figure 14: Status of an anionic flocculant molecule in solution (schematic). (A): in water, the molecule is extended and has an en-to-end length of L. (B): molecule in high ionic strength solution. L is now reduced to L_1 by coiling up of the molecule and $L_1 < L$. (C): screening of the functional group by crowding of ions in a high ionic strength solution.

5) The status of cations

The slurry contains hydrolysable cations including Al^{3+} in the form of AlO_2^-. If present or extraneously added, most of such ions will form hydrated oxides and higher alkali-ionized species.

In this medium, cations reach their highest level of hydrolysis. For example all of the Al^{3+} form a mixture of hydrated alumina [namely, $Al(OH)_3$) and aluminate $Al(OH)_4^-$]. Iron generates numerous monomeric and polymeric ionic species, albeit the high-pH ones are anionic. The same is true for most of the cations available in the medium. Ca^{2+} on the other hand is less readily hydrated and as can be seen from Figure 15, at the alkaline pH values predominating in the WSRC slurry it has cationic hydrolysis species. This implies that if $CaCl_2$ salt solutions were to be added to the slurry prior to anionic flocculant addition, there is a good probability that flocculation would be "activated" by the calcium species. Thus, anionic flocculant adsorption would be enhanced.

XVI. Special Status of Emulsion-Type Polymers

In these commercial products, the polymeric flocculant is initially dissolved in water and then emulsified in oil (O/W emulsion). When a quantity of such a product is added to an agitated slurry, initially, the flocculant solution is isolated form the aqueous environment, by a thin layer of mineral oil. Such oily droplets are not significantly affected by the high pH and high ion concentration of the aqueous environment. When the emulsion breaks and the aqueous phase is released, the flocculant molecules will be subject to the same

Figure 15: Speciation diagram for Ca^{2+} by pH. Total species concentration: 10^{-3} Mol/L

kind of changes of coiling and screening effects. However, under the right agitation regime many of the flocculant-containing droplets will collide with the particle walls and release polymeric molecules which have a higher probability of adsorbing. Under these conditions the "ion screening effect" can be expected to be at its minimum since adsorption precedes exposure to the ionic medium. Polymer-solid binding will occur by the agency of
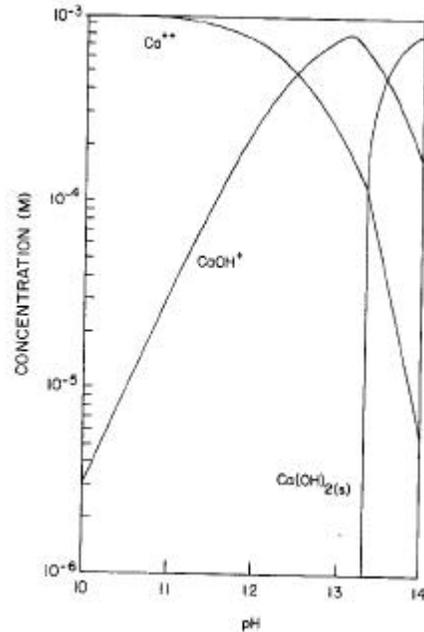
-hydrophobic bonding
-non-ionic adsorption (hydrogen-bonding) and
-activation by the agency of polyvalent cations such as Ca^{2+}.
Such a flocculant system, in the short term, will be less adversely affected by the
high-pH of the medium.

This likely scenario is schematically illustrated in Figure 16.

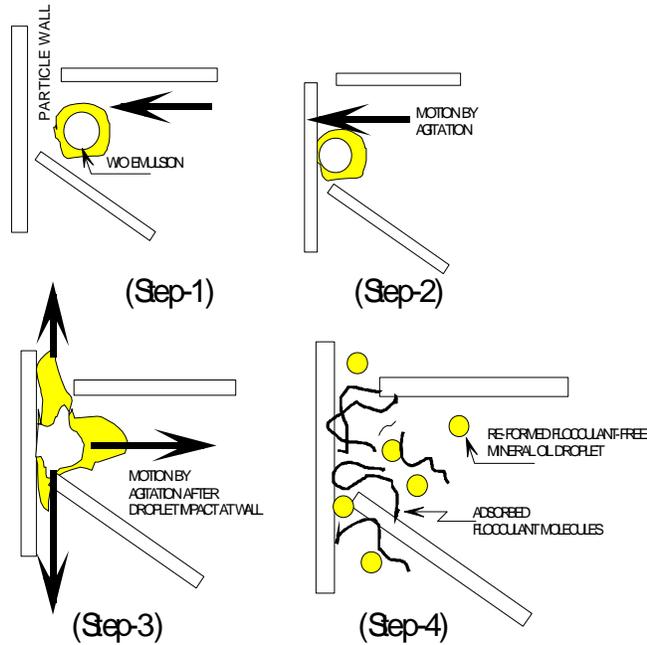Figure 16: The action mechanism of emulsion type flocculant
formulations. Steps-1 and 2: Flocculant addition under intense
agitation. Emulsion droplets accelerate towards the solid
particle and collide with it. Steps-3 and 4 : The emulsion droplet
releases its aqueous solution of flocculant molecules which act
as flocculation-bridges, and the mineral oil forms droplets that
disperse in the aqueous slurry.

XVII. Preferable Approach to Testing The Flocculation-Filtration Process

Flocculation and filtration tests conducted to-date by WSRC researchers, have been only marginally successful. It is possible however, to use the information and observations given in the preceding pages, to further-optimize the flocculation-filtration process. Such an approach should include the following operational steps.

1) Optimize flocculant dose under a randomly selected, constant mixing regime.
2) Select a performing flocculant and re-optimize the mixing regime with the selected flocculant at 5 dosage levels (5 data-points).
3) At the newly-established optimal flocculant dose and mixing regime, allow the flocculated slurry to sediment and produce a clear supernatant solution.
4) Filter the supernatant solution and the sediment separately.
5) Run experiments to see if filtration-aids and surfactants produce desirable acceleration of the filtration rate. Use filtration aids with the sediment only, not the total slurry. Filtration aids may not have much effect on the total slurry or supernatant liquor itself if it were to be subjected to a polishing filtration step, because the quantities of surfactant needed to reduce the surface tension of such a slurry, with so much salt around, may be prohibitive due to "micellization phenomena".

This scheme is outlined in Figure 17.

We need to note that while the approach given in this schematic diagram may appear to have many processing vessels which may result in a requirement to for an added floor-space. It does not. It is an explanation of the concept of the process. In reality the equipment to be used in implementing this scheme are less numerous and should not create needs for an expanded floor area. An explanation is given below.

By referring to Figure 17 we can make the following observations:

a) high shear and slow agitation steps can be accomplished in a single compact unit. Such combined highly compact units are commercially available.
b) a thickener is essential, as part of the whole concept of using flocculants. Again, high-capacity small floor-space thickeners are currently available on the market. In fact there are very compact equipment that incorporate high shear flocculation, low shear agitation and thickening in a single unit.
c) filtration cake washing is indeed a necessary step in any filtration process of this nature. Most plant-size filtration devices, such as rotary filters actually incorporate a washing step as part of the overall filtration process.
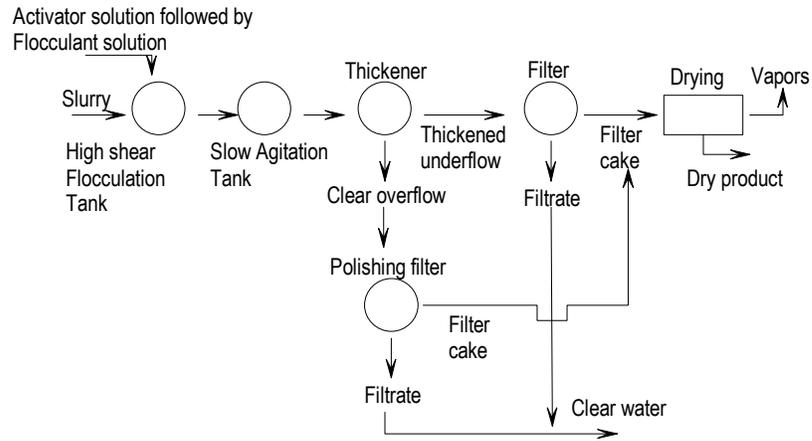
Figure 17: Schematic explanation of the flocculation filtration scheme that may prove successful in the flocculation-dewatering of WSRC sludge

Therefore, space considerations should not be of concern.

To reiterate, we need to reconcile the fact that flocculants need to be used as intended; that is, a flocculation process needs to go through the steps of Flocculate $\Rightarrow$ Sediment $\Rightarrow$ Filter in two steps; one for supernate, one for flocculated sediment.

It will be prudent, in the case of WSRC slurries, to test the utility of Ca^{2+} in the form of $CaCl_2$ prior to flocculant addition. This will facilitate anionic flocculant-anchoring to the particle walls that are most likely, negatively charged at such a high pH. Simultaneously, non-ionic, (likely $-NH_2$) groups will adsorb on non-ionized surface sites of the solids contained in the slurry. Therefore a copolymer such as (Alclar 662 or any of the emulsion formulations shown in Table-9) or a 1:1 mixture of anionic and non-ionic polymers (e.g.: Alclar 600 and Alclar 662) could be used with the same end result, which will be good flocculation.
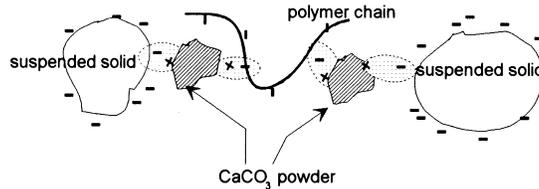

Figure 18: Action of $CaCO_3$ powder as flocculation activator (schematic)

Table-9 : Some of the flocculants used in the WSRC tests and their properties

Flocculant	Chemistry	Dispensed as	pH 1% solution	significant extras in formulation
Alclar-600	Homopolymer, sodium acrylate	powder	9	acrylic acid impurity 0.2 % borax
Alclar-662	Copolymer of acrylamide and sodium polyacrylate	powder	6	acrylic acid impurity
Superfloc HX-2000	Modified polyacrylamide	W/O emulsion	1.2% NaOH 3.1% NH$_3$	20% petroleum oil
Superfloc HX-400	Modified polyacrylamide emulsion	Emulsion	2.1 % NaOH	
Superfloc HX-300	Modified polyacrylamide emulsion Anionic polyacrylamide	Emulsion	2.2 % NaOH	10-25 % petroleum distillate 0-11.9 %mineral seal oil 2% NH$_3$
Superfloc HX-200	Modified polyacrylamide emulsion Anionic polyacrylamide	Emulsion	2.5 %	11-25 % petroleum distillate 0-14 %mineral seal oil 2.1 % NH$_3$

Since the final filter cake is destined for vitrification, $CaCl_2$ could be preferably substituted by $CaCO_3$ powder. In this case the powder should be of "pulverized calcite mineral" rather than commercially available pure, precipitated $CaCO_3$. The flocculated thickener underflow thus obtained, will be a much-les gelatinous product which would filter at the desired high rates.

The mode of action of calcite powder is similar to that of Ca^{2+} that was given in Figure 10 and is shown here in Figure 18.

XVIII. Concluding Comments and Further Recommendations for Future Direction

Despite the fact that the WSRC slurry contains high salt concentrations and exhibits high pH, these conditions can be put to beneficial use in the flocculation process.

Among the flocculants used by WSRC researchers, shown in Table-9, Superfloc HX-200 and 300 at a single, fixed dose level have produced limited, visible improvement in filter performance tests. These flocculants should be optimized with respect to dose and agitation regime.

The fact that these two flocculants are emulsion-type formulations, support the model shown in Figure 16 and the discussion in section **XVI** above. Also, the fact

that they carry anionic and non-ionic functional groups on the same molecular chain, promises that bonding to ionized and non-ionized solid surface sites will be enhanced.

Tests with $CaCl_2$ and $CaCO_3$ using emulsion-type-mixed functional group flocculants such as Superfloc HX-200 and 300 should definitely be conducted.

Commercially-available flocculants are successfully used in aggressive chemical environments comparable to those of the WSRC sludge, for example in the filtration of red-mud in the production of alumina from bauxite. Future tests, need not seek new, magic-flocculants other than those, subjected to limited testing at WSRC so far. Rather, a comprehensive protocol for their testing needs to be followed.

The procedure for a future test program, if it were to be conducted at the author's laboratory, at the Colorado School of Mines would include the following, to meet the targets that need to be accomplished.

In a second phase of the project the following test sequence will be followed in order to achieve the outcomes sought:

1) We will conduct the flocculation/filtration tests under a proper protocol which incorporates the steps of high shear/followed by low shear flocculation, followed by time for sedimentation followed by filtration rate testing. The filtration will need to be made for the clear supernate and the sediment in parallel.

2) We will conduct separate filtration tests on the clear supernate and the flocculated sediment. This should decrease the overall time spent on treating a given volume of initial slurry at full-scale application conditions.

3) We will optimize flocculant selection and dosage. To this end I have already found that flocculants successfully used in the alumina industry (red-mud filtration) are good candidates for testing in this system. Emulsion-type co-polymeric products are at the top of the candidate list for testing. The optimization process will run at least 5 doses of the candidate flocculant at various agitation regimes till the optimal conditions are established.

4) We will use calcium and if approved, calcium carbonate mineral powders as activators for flocculant adsorption in this high-ionic-strength medium. Particularly calcite, is a promising additive which should improve filtration rates of the sediments via increasing filter cake porosity.

5) We will incorporate a filter-cake washing step to the testing process.

6) We will select and use filter aids in the filtration of the sediment.

7) We will look at dilution as a sedimentation/filtration improving step. The approach in this aspect of testing will be as follows:
   a) Allow original slurry to sediment by coagulation; we have observed in our laboratory, that it does coagulate on standing on its own, as predicted by the scientific basis of coagulation processes.
   b) filter the supernate alone without modification

c) take the sediment which is, now, low in volume and has manageable quantities of dissolved salt and re-slurry it (possibly using filter cake wash water). This will dilute the salt content of the new slurry, which would make it a well-behaved, low-salt content system suitable for flocculation an accelerated filtration.

d) flocculate, under optimal conditions, and filter this new product according to the protocol established.

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