COMPARATIVE STUDY OF FLOCCULANTS ON THE SEDIMENTATION RATE OF SILICA FOR WAIRAKEI AND BROADLANDS GEOTHERMAL WASTE WATER

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ABSTRACT

The synthetic flocculants are polymers based on acrylamide and its copolymers. These are composed of nonionic, cationic and anionic charged formulas which are primarily produced for filtration processes and waste water clarification. The effect on sedimentation rate and flocculation of silica with the presence of inorganic electrolytes and in combination with the organic polymer flocculants were measured using a turbidimeter.

The cationic polymers were found to coagulate silica rapidly in geothermal liquid at concentrations of 5-20 ppm. The silica aggregates were formed by a rapid irreversible reaction which produced smaller particle aggregates that did not settle. An increase in turbidity correlates to the increasing charge of the cationic polymers. The anionic polymers did not increase aggregation when applied alone, but they did increase the settling rate of previously aggregated silica.

The aggregation is initiated by adding polyaluminum chloride and flocculation is enhanced by adding anionic polymers. Flocculation is also enhanced by anionic polymers when combined with magnesium chloride. The nonionic polymer tends to stabilize the aggregated silica particles formed by polyaluminum chloride but also enhances the flocculation when combined with magnesium chloride. The aggregation of silica is increased by addition of polyaluminum chloride, $FeCl_3$ and $Ca(OH)_2$ at concentrations as low as 5 ppm. Rapid flocculation (less than 30 minutes settling) of silica occurred by addition of 200 ppm polyaluminum chloride or 50 ppm lime (ppm as Ca). $MgCl_2$ increased the flocculation at 300 ppm Mg. There was no enhancement of flocculation using $CaCl_2$ alone for the range of concentrations (20-300 ppm) tested.

1.0 INTRODUCTION

1.1 Situation

Disposal of waste water from geothermal wells is one of the major concerns during the exploration, development and production stages of geothermal fields. The reservoir management strategy involves a balance between environmental constraints, energy optimization and reservoir maintenance. During discharge testing of newly drilled **wells** at the exploration or development stage, the separated waters, are either discharged to the environment or reinjected through injection wells. Depending on fluid chemistry, pretreatment of the waste water may be required even at this stage to minimize deposition of polymerized silica in the injection wells. Aging of this waste in temporary ponds and dropping the temperature does not guarantee removal of silica since the colloidal silica particles formed tend to remain in stable suspension especially with **a** rapid drop in temperature where the particle sizes tend to become smaller (Brown, 1995 PNOC-EDC Lecture). Without pretreatment or flocculation to remove silica, deposition in the surrounding formation of reinjection wells may result especially where downhole temperatures are low.

The separation temperature for,extraction of steam is limited by the amorphous silica saturation in the liquid (say about 200°C flash temperature for >300°C reservoir) in order to minimize scaling in the surface facilities and possibly in the injection wells. For a reservoir temperature of 300°C flashed to a separation temperature of 200°C, the remaining heat energy from the liquid at 200-100°C is about 40% of the total energy from the two phase fluid (Harper and Thain, 1992). Further utilization of this extractable energy above the amorphous silica saturation (fluid is highly saturated in silica) requires some Pretreatment of fluid ta prevent potential problem by silica scaling.

Harper and Thain. (1992) propose a development strategy for efficient use of the geothermal fluid energy. This includes further utilization of the separated water from the primary flash plant for binary type electrical power generation, which is currently being done at Kawerau, followed by extraction of the silica from the waste water with some pretreatment of fluids to obtain silica products which have commercial value. However this pretreatment process occurs downstream of the binary plant hence some problems of scaling in the heat exchanger may exist (1995 Kawerau field trip). Use of binary type system to extract more heat in some high temperature geothermal areas in the Phillippines (Bacon-Manito and Leyte) is currently being considered and developed (Barnet and Garcia, 1993).

Flashing of geothermal fluid to atmospheric condition may give an added advantage of decreasing the volume of separated mater to be injected to the well. This will minimize cost of drilling additional wells to meet the injection water capacity requirement and minimize reinjection returns to the production sector. However, the problem of disposing the solid silica product exists. Precipitation and removal of silica as a means to control scaling yields solid products with no commercial value except as a landfill. Practical knowledge and experience in getting a desirable silica product is still limited. At Wairakei, a large amount of silica is deposited along a discharge canal and this is removed regularly. The development and operation of a binary type power plant like Botong (Bacon-Manito), where the silica content in atmospheric separated mater is about 1400 mg/kg (Barnet and Garcia, 1993) also results in large quantities of silica solids. These are some of the potential sources for extractable geothermal silica products with commercial value that can be used as additives in the processing of paper, paint, cosmetics, rubber and other related industries. The extraction of silica from geothermal liquid requires pretreatment and process control to obtain the optional particle size for industrial applications.

Large scale development of geothermal fields in the Philippines like Leyte have the problem of disposing large quantities of geothermal waste water. Other methods to dispose this waste water may be considered such as reverse osmosis to convert the geothermal water into potable water suitable for domestic use or disposal to the environment. However, this process requires silica concentration of less than 100 mglkg in the pretreatment process which is below the silica solubility at this temperature..

1.2 Methods to Control Deposition and Silica scaling

The choice of method to control silica scaling or the type of geothermal development to be adopted will depend on the type of fluids (chemistry and temperature) of the geothermal systems and the constraints on the environment. Several methods to cope with silica scaling were outlined by Brown (1995) which are: 1.) Avoidance *of Supersaturation* - this limits the Separation temperature of the two-phase fluid for extracting steam within the amorphous silica solubility. Scaling will not be a problem if the separated water is undersaturated with respect to amorphous silica at the separation temperature. One option is to have double flash system where the removal of CO_2 gas is maximized and the pH of separated water is increased thus increasing the solubility of amorphous silica. Avoidance of silica saturation could introduce additional capital cost in the fluid collection and disposal set-up. *2.) Inhibition of colloid formation* - lowering of pH (e.g. pH 5) will decrease the rate of colloidal silica formation. though silica will polymerize and deposit eventually. The pH modification has been successful even in highly saline water such as in Salton Sea Unit 2 (Hoyer et. al 1991). 3.) *Aging of the water* - silica is allowed to become fully polymerized at constant temperature to produce a soft removable silica scale. *4.) Colloidal stabilization* - use of organic polymer dispersant to prevent agglomeration of silica. This is currently being studied in the Philippines (Barnet and Garcia, 1993). 5.) *Removal of* silica – use of chemical flocculant to induce colloidal silica formation and precipitation. This method has been successful in Cerro Prieto using lime as flocculant (Hurtado et. al 1989). 6.) *Raising the pH* - addition of caustic soda to increase the pH of water. This method is effective but costly as shown by test experiment at Broadlands (Brown and McDowel, 1983).

1.3 Scope and Objective of Study

A set of experiments were conducted to compare the effects of inorganic polyelectrolytes and synthetic polymer flocculants on the aggregation and flocculation of colloidal silica particles at room temperature.

This will help identify the type of electrolytes or organic polymers to be used for future applications in the control of colloidal particle size and flocculation for silica removal in geothermal liquids. Actual conditions in the field where there is a variable range in fluid chemistry and temperature require different concentrations of flocculants depending on the type of applications. The time available for the monitoring of turbidity was limited and the observations and results of these laboratory tests may differ with actual field testing.

The flocculants mere tested individually on their effect in forming aggregates of silica particles and in enhancing flocculation when used alone at 5 and 20 ppm concentration. The dosing concentration of inorganic flocculants (magnesium chloride, calcium chloride, polyaluminum chloride. calcium hydroxide and femc chloride where further tested above *20* ppm to evaluate the minimum concentration where rapid flocculation (less than **20** minutes settling time) may occur. The single flocculant dosing is for applications requiring removal **of** silica by settling without the required **uniform** particle *size.* Due to limited time. the polymer flocculants were not tested at concentrations below 5 ppm.

The organic polymer flocculants were combined with the divalent cation Mg^{+2} and the trivalent Al^{+3} to test their effect in increasing flocculation rate. It has been thought that the nonionic and anionic polyacrylamide flocculants require the presence of divalent cations in solution for ionic bonding to increase adsorption of polymer to colloidal silica particles. **This** effect is compared between magnesium chloride and polyaluminum chloride in combination with the organic polymers. In some applications where there is a requirement for a specific particle size of silica, the inorganic electrolytes are added first to aggregate the silica particle **and** then combined **mith the** organic polymers to flocculate the aggregated particles for increased concentration and recovery. The combination of inorganic flocculants **with** the polymers will help evaluate this objective. .

1.4 Flocculants

1.41 Solid/liquid dispersion

To understand the terms used in this study with respect to the states of solid-liquid dispersion. is best illustrated in Figure 1 (from Tadros. 1987):

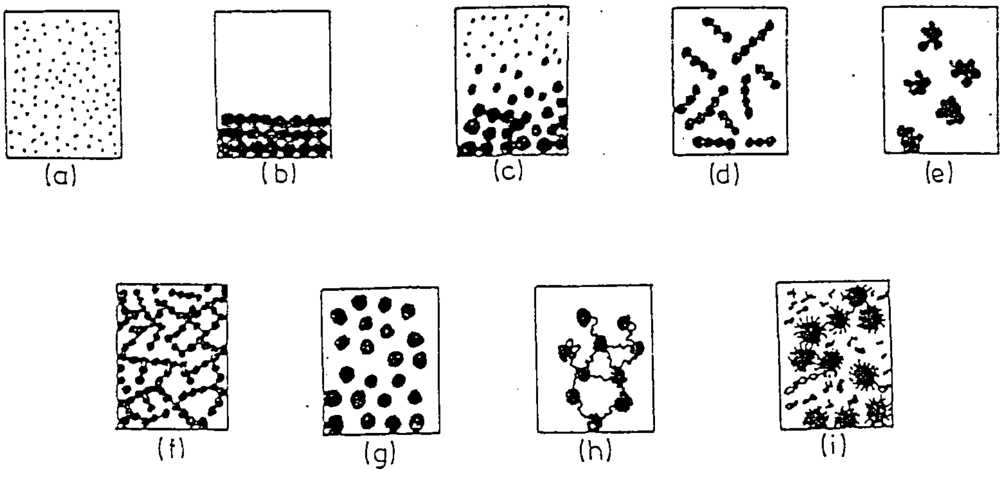

Figure 1. Schematic representation of the state of dispersion: (a) colloidally stable suspension with ***no*** *settling; (b) colloidally stable clayed suspension (uniform particle size); (c) colloidally stable clayed suspension (polydisperse); (d) coagulated suspension: (e) coagulated suspension with compact clusters; (f) coagulated suspension at* ***high*** *volume fraction; (g) weakly flocculated suspension; (h) flocculated suspension by polymer bridging; (i) weakly flocculated suspension by free polymer (depletion flocculation). (from Tadros, 1987)*

Colloidal silica particle is initially in the form (a) which is derived from polymerization of saturated silica in the liquid Several particles combine or associate to form aggregates. The formation of several aggregates by particle bridging which results in settling is known as flocculation Addition of flocculants could result in the formation of either aggregates or flocculated silica particles similar to (c) to (i).

1.42 Flocculants vs. Dispersants

Flocculants or coagulants are used to aggregate fine particles or liquid droplets in aqueous media to improve separation of the two components. Flocculants function by charge neutralization, double-layer compression, particle bridging, or by forming large nets that engulf masses of particles called sweep flocculation (Hann, 1993). Dispersants normally function by charge repulsion, steric repulsion, or both. Some polymer flocculants are chemically similar to dispersants and differ only in molecular weight and dosage level. Dispersants are normally anionic character of lower molecular weight and higher charge density than polymeric flocculants.

1.13 Flocculation of silica particles

Being a highly negative charged surface particle, formation of colloidal silica or its flocculation is influenced by the cations especially di- and trivalent cations which act as bridge between neighboring colloid particles. The combined particle then coagulate or flocculate out of solution due to their increase in molecular weight. The cations such as Fe^{+3}, Al^{+3}, Mg^{+2} and Ca^{+2} can contribute to this type of deposition. The adsorption mechanism of the polymer or polyelectrolytes to the silica particle involves hydrogen bonding between hydroxyl group on the oxide surface and the amide group of the polyacrylamide to form as bridge. When the silanol group on the silica surface are eliminated, these polymers can no longer adsorb silica particles (Gregory, 1987). Adsorption for anionic polymers and the negatively charge surface of silica particle *requires* certain concentration of divalent metal ions such as calcium and magnesium to promote adsorption called ion binding. These cations are known to bind strongly to carboxylate groups such as those on hydrolyzed polyacrylamide. These cations may also link with the negative side of the silica particle. The kinetic aspects of the polymer flocculation are shown on Figure 2 (Gregory, 1987) and involve the following steps:

(a) mixing of the polymer molecules among the particles to give a uniform distribution:
(b) adsorption of the polymer on the particle surface
(c) rearrangement of adsorbed chains to give an equilibrium configuration;
(d) collision between particles with adsorbed polymer to form aggregates or flocs
(e) break-up of flocs

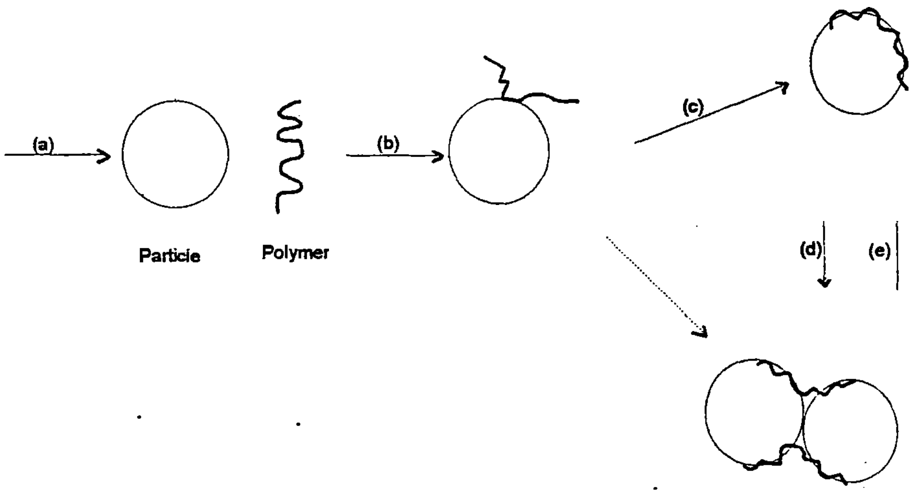

Figure 2. Kinetics of polymer adsorption and flocculation (modified from Gregory, 1987)

1.44 Nature of Flocculants

From the definition by Gregory (1957) - 'Effective flocculants are usually linear polymers. often of high molecular weight, whch may be nonionic, anionic or cationic in character.' Polyacrylamide is nominally nonionic character. Most commercial polyacrylamide based synthetic flocculants are derived from controlled **hydrolysis** of acrylamide to obtain very **high** molecular weight (up to 2×10^7) with different degree of anionic character or charge density. Cationic polyacrylamide based flocculants are also prepared by a similar process but use cationic monomer and acrylamide copolymerization. The proportion' of cationic monomer determines the cationic charge density of ionic polymers, termed polyelectrolytes. Inorganic **flocculants** such as iron and aluminum salts, which form complex polynuclear species, could also be called polymeric and' polyelectrolytes. Prepolymerized products such as polyaluminum chloride are now commercially available. Some examples of synthetic polymeric flocculants are as follows (Gregory, **1987):**

nonionic:	polyvinyl alcohol, polyethylene oxide
anionic :	sodium polystyrene sulfonate
cationic:	polyethyleneimine, polydiallyldimethylammonium chloride ("Catfloc"), poly(2-vinyllimidazoline)

1.45 Flocculants Tested

The inorganic polyelectrolytes tested are magnesium chloride, calcium chloride, calcium hydroxide or lime, femc chloride and polyaluminum chloride or PAC. The synthetic organic polyelectrolyte tested are **high** molecular weight, water soluble polymers and copolymers **based** on accrylamide. These polymers are used for municipal sewage and industrial waste water treatment such as in **primary** sedimentation, secondary sedimentation sludge thickening sludge flotation, filtration and dewatering process. The **following** are the recommended normal dosage:

Sedimentation/Settlement	: 0.5 - 5 mg/liter
Sludge Thickening	: 5.0 - 20.0 mg/l
Sludge Flotation	: 5.0 - 20.0 mg/l
Sludge dewatering	: 2.5 - 5.0 kg/ton dry solids

TABLE 1 POLYMER FLOCCULANTS TECHNICAL DATA (FROM ALLIED COLLOLDS)

Product	*Ionic charge*	*Molecular weight range*	*Effective pH range*	*Principal Applications*
ZETXG 45	Cationic INCREASING CATIONIC CHARGE ↓	4	4-9	PC, C
ZETAG 92	Cationic	5	4-9	PC. CF
ZETAG 63	Cationic	3	4-9	FP, BP, C, RVF, F
ZETAG **57**	Cationic	3	4-9	FP, C, **RVF.** F
MAGXAFLOC 351	Nonionic	5	5-11	PC, PR
MAGNAFLOC **E24**	Anionic INCREASING ANIONIC CHARGE ↓	4	5-11	PC, PR
MAGNAFLOC 155	Anionic	5	5-11	PC, PR
MAGNAFLOC 1011	Anionic	5	**5-11**	PC, PR
MAGNAFLOC 156	**Anionic**	5	5-11	PC. PR
MAGNAFLOC 919	Anionic	5	5-11	PC. PR

Notes:

Molecular **weight** scale: 1-5, where 1 = 0.5-1.0 million and 5 = 15-20 million

Application: **PC - Primary** clarification PR - Phosphate removal ***C*** - Centrifuge
F- flotation **RVF** - Rotary vacuum filter **BP** - Belt press

Zerag and Magnafloc are trade marks of Allied Colloids (Australia Pty. limited)

1.5 Turbidimetry

During agglomeration,' the particle size could reach above 50nm which can be detected by less sensitive methods such as turbidity. The turbidity method could provide measurement on the settling fate of the flocculated particle. This is a simplified and rapid determination which operates on the principle of light scattering by the particles in suspension or the Tyndall effect. The amount of scattered light measured at right angle to the light source is proportional to the volume or number of particles in the 'suspension and will also depend on 'the relative refractive index and wavelength of the light source. The turbidity measurement will indicate degree of agglomeration while the particle *size* analyzer will show the colloid formation not seen in turbidity measurement. This is the method used in this *study* to determine the effect of flocculants on the flocculation rate of silica particles in geothermal water.

2.0 EXPERIMENTAL METHODS

2.1 Equipment

Coagulation and Flocculation Simulator - This equipment is composed of six units of retractable paddle stirrers, six pieces of clear plastic sedimentation jars and bottom light source to illuminate the test solutions or **suspension.** The stirrers are electronically controlled with programmable speed which ranges **from** 30 to 300 rpm. Brand /Model: BOLTAC/Series 675,.serial No. 910164.

Turbidimeter - *An* analogue *scale* single standard calibration meter. This operates on the principle of light scattering of non-coherent or visible light source by the colloidal particle in the solution **(Tyndall** effect) measured perpendicular to the source of light. The intensity of scattered light is correlated to the **turbidity** of the **solution.** The meter is first calibrated using a standard mith known turbidity values specific for this instrument model to read at full scale deflection (say 100 units). The sample is then analyzed by transferring it to the cylindrical glass cell and placing it in the, cell compartment. The amount of turbidity is read directly from the scale which is in NTU **units.** The standard ranges from 0-1, 0-10, 0-100 and 0-1000 NTU. Brand/Model: HACH/ Model 2100A with cell riser for 0-100 and 0-1000 NTU *standards.*

2.2 Water Sampling

Separated water samples were taken downstream of the weirbox and a holding pond at well BR48, **Broadlands, Ohaaki..** The water temperature ranged from 80°C below the weirbox to 35°C at the pond Samples were collected into 20-liter plastic container and **transported** to the Wairakei laboratory. Water samples for Wairakei atmospheric separated water were taken **fiom** an atmospheric separated water pipeline near the pilot test plant facility. The water was cooled down to 40°C by heat exchanger during collection.

2.3 Preparation of Stock Solutions

Stock solutions of 10,000 ppm or 10 mg/ml were prepared for the following inorganic electrolytes:

Magnesium chloride - 10 **mg/ml** as Mg, prepared from $MgCl_2.6H_2O$ crystals
Calcium chloride - 10 mg/ml as Ca, prepared from $CaCl_2.2H_2O$ crystals.
Calcium hydroxide - **10 mg/ml** as Ca, prepared from 96% $Ca(OH)_2$ powder
Ferric Chloride - 10 mg/ml as $FeCl_3$
Polyaluminum chloride (PAC) - 10 mg/ml as PAC prepared from 32 g/ml concentrated solution (**fiom** Drew New Zealand Ltd)

The cationic and anionic polyelectrolytes and nonionic polymer were prepared from solid beads samples. To a 200 ml dry plastic bottle, 0.4 grams of solid beads were transferred and 5 ml ethanol were added as wetting agent. Then 195 ml of distilled water were added and the mixture was shaken every 30 minutes until dissolved The final solution contained 0.1% or 1 mg/ml of the active ingredient.

2.4 Flocculation **and** Sedimentation rate Procedure

To determine the effects of organic polymers and inorganic electrolytes. they were added to geothermal liquid either as a single individual electrolyte or as a combination of inorganic electrolytes such as Mg^{-3} and Al^{-3} with the organic polymers. The inorganic electrolytes were added first to promote aggregation of silica particles then the organic flocculants were added to induce flocculation or settling. The rate of settling was monitored during a **period** by analyzing the turbidity of samples from the upper and bottom portion of the jar. In some cases where settling of precipitate had occurred the bottom samples were not analyzed for turbidity.

The water samples (1 liter volume) were first transferred to the sedimentation jars. and the initial turbidity was determined for the untreated water. The water samples were then stirred for 2-5 minutes while adding known amounts of the stock test solution to obtain a desired final concentration in the test solution. The stirring was stopped and the flocculated particles were allowed to settle. The tests were initially conducted using flocculant concentrations of 5 ppni and 20 ppm. Further tests using higher dosage were complemented to obtain minimum concentration of simple electrolytes required for flocculation.

3.0 RESULTS AND DISCUSSIONS

3.1 Result of water sampling

The water samples collected at the holding pond near BR 48 had been aged Minor cloudiness in the deeper portion of the pond suggested that colloidal silica and colloidal sulfur had formed The total silica content of the untreated sample was 700 ppin SiO_2 For the tests. water samples were taken from atmospheric separated waterline after about 40m from the weirbox. The sampling temperature range from 80-85°C and the total silica of 740 ppm. Atmospheric separated water from Wairakei was cooled to 40°C during sampling. The total silica of this fluid is about 500 ppm $SiO2$. There was no control on the aging time of the fluid since fluid samples stored up to 4-5 days were used Untreated samples were monitored and stored under the same conditions **as** treated samples to assess background effects: these turned out to be very minor.

3.2 **Performance of** Individual **Flocculants on** Turbidity

3.21 Synthetic polymers

The first set' of tests assessed changes in turbidih as a measure of silica aggregation using concentrations of 5 and 20 ppm. The cationic polymers produced very rapid formation of long, coagulated mucus like precipitates which stuck to the stirrer blades. The effect was strong at 20 ppm and minor at 5 ppm for all flocculants. The precipitate did not break up by agitation indicating that the process was irreversible. The turbidity of suspension increased compared to the untreated fluid indicating formation of more aggregated silica. This was the observation made on all four Zetag (Z 92, **57,** 63, 45) cationic flocculants for BR 48 fluids. There was no further change in turbidity up to about 100 minutes after the addition of the flocculants. Polyaluminum chloride which was added to the batch also showed minor increase in turbidity indicating aggregate formation even at 5 ppm concentration: For the anionic and non-ionic flocculant tested at the similar conditions above. only Magnafloc E24 showed minor increase in the turbidity while the rest did not change the turbidih as compared to the untreated fluid. The order of decreasing effect on turbidity for cationic flocculants is as follows: Z 63 > Z57 > **Z 92** > Z45>PAC. The turbidity plot versus time of the cationic flocculants are shown in Figure 3 and the results are tabulated in Table **2.** The turbidity **data** are from the top portion of the jar. There is no significant difference between the top and bottom turbidity measurement during these tests. The nonionic and anionic polymers were not included in the plot since there was no change in turbidity when adding these flocculants.

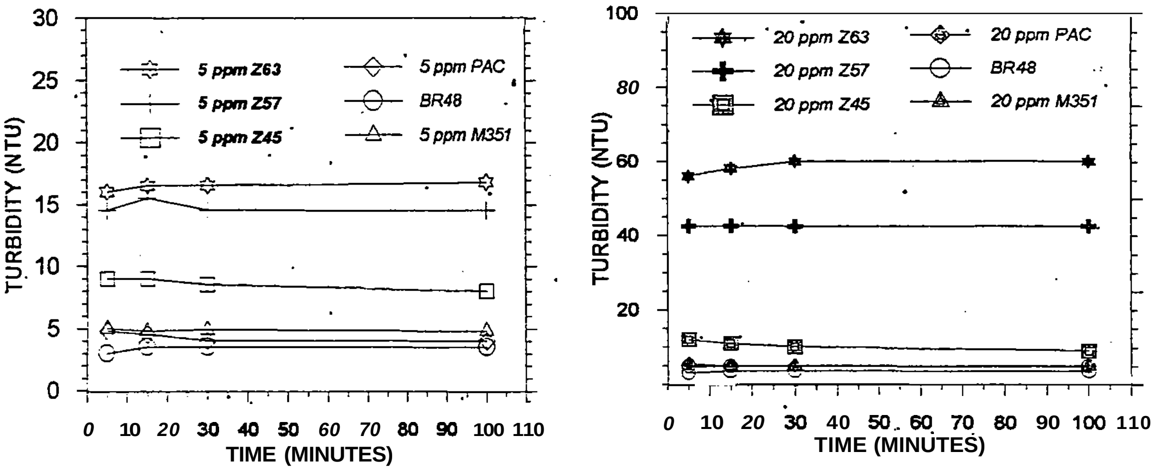

Figure 3. Effect of polymer flocculants at 5 and 20 ppm concentrations on turbidity of BR 38 water

TABLE 2. EFFECT OF FLOCCULANTS ON TURBIDITY OF BR48 WATER

Flocculant	*Conc.*	*Turbidity (NTU)*				*pH*
	(ppm)	*5 min.*	*15 min.*	*30 min.*	*100 min.*	
Z 92	5	5	5	5	5	9.15
Z 57	5	14.5	15.5	14.5	14.5	9.16
Z63	5	16.0	16.5	16.5	16.8	9.17
PAC	5	4.8	4.5	4.0	4.0	9.16
Z 92	20	6.8	6.8	7.0	7.0	9.16
Z 57	20	42.5	42.5	42.5	42.3	9.16
Z 63	20	56	58	60	60	9.17
PAC	20	5.5	5.0	5.0	5.0	9.12
BR48(8-11SEP95)		3.0	3.5	3.5	3.5	9.17
Z 45	5	9.0	9.0	8.5	8.0	9.17
Z 45	20	12	11	10	9.0	9.19
Z 45	40	13	12	12	12	9.18
M 351	5	5.0	4.8	4.9	4.8	9.18
M 351	20	4.8	5.0	4.8	4.8	9.18
M 351	40	4.8	4.9	4.8	4.8	9.18
BR 48(8-12SEP95)		4.8	-		4.8	9.18
M E24	5	7.5	-	7.5	-	9.20
M E24	20	7.0	-	7.0	-	9.20
M 155	5	6.5	-	6.5	-	9.20
M 155	20	6.4	-	6.5	-	9.20
M 1011	5	6.5	-	6.5	-	9.20
M 1011	20	6.5	-	6.5	-	9.20
M 156	5	6.5	-	6.5	-	9.20
M 156	20	6.5	-	6.5	-	9.20
M 919	5	6.5-	-	6.5	-	9.20
M 919	20	6.5	-	6.5	-	9.20
BR48 (8-12SEP95)		6.5	-	6.5	-	9.20

Notes: Z - Zetag; M - Magnafloc; PAC - Polyaluminum chloride
Temperature = 20-25 °C Source : Top of the jar

Flocculant	*Concentration (ppm)*	*Turbidity (NTU)*	*pH (21 °C)*
Z 45	20	2.2	8.77
Z 92	20	1.7	8.78
Z 63	20	19	8.78
Z 57	20.	7.5	. 8.77
UNTREATED	0	0.9	8.77
Z 92	1	1.32	8.78
Z 92	. . 15	1.35	8.75
UNTREATED	0	1.00	8.78

The cationic polymers were also tested using Wairakei water samples at **20** ppm concentrations (Table 3). Similar observations were made of rapid formation of long gelatinous precipitate and increase in fluid turbidity. The decreasing order on the effect of turbidity of the cationic polymers are as follows: Z **63** > Z **57** > **Z45** > **Z 92.** Since **Z** 92 had the lowest turbidity effect on Wairakei water, concentrations of **<20** ppm nere used to further assess effects on turbidity. The results showed an increase in turbidity **from** 1. NTU for untreated water to 1.35 NTU for concentrations of 1, **5,** 10, and 15 ppm Z 92 (Table 3). Turbidity measurements were taken from top portion of the jar after **10** minutes flocculation. **This may** indicate an enhancement in aggregation of silica at lower *than* 1 **ppm** concentration.

3.22 Inorganic Flocculants

The concentration of femc chloride **and** PAC used in **this** comparison are expressed in their formula weight form (e.g. as ppni PAC or ppm $FeCl_3$ not as ppm Fe or **ppm** Al) unlike the other **flocculants** like calcium chloride and magnesium chloride which are expressed **as** ppm Ca and ppm Mg respectively. This may lead to some discrepancy in terms of the concentration units used however, the same terms are used throughout the following discussions.

For the tests of the **5** inorganic **flocculants** ($MgCl_2$, $CaCl_2$, $Ca(OH)_2$, PAC **and** $FeCl_3$) at 5 and *20* ppm concentration (Table 4), **only** calcium chloride and magnesium chloride had no **effect on** turbidity while calcium hydroxide [$Ca(OH)_2$], polyaluminum chloride (PAC) and femc chloride increased the turbidity of the suspension. The following is the decreasing effect of inorganic flocculants on the turbidity of the geothermal water samples applied to BR48 fluid: $FeCl_3$ > $Ca(OH)_2$ > PAC > $MgCl_2$ > $CaCl_2$.

TABLE 4. EFFECT OF INORGANIC FLOCCULANT ON THE TURBIDITY OF BR 48 WATER

Flocculant	*Concentration*	*Turbidity (NTU)**		*pH*
		5-10min.	*30-40min*	*25-26 °C*
$MgCl_2$	5 ppm Mg	1.8	1.8	8.76
$MgCl_2$	20 ppm Mg	1.8	1.8	8.76
$CaCl_2$	5 ppm Ca	1.7	1.7	8.76
$CaCl_2$	20 ppm Ca	1.7	1.7	8.76
$Ca(OH)_2$	5 ppm Ca	3.1	5	8.9
$Ca(OH)_2$	20 ppm Ca	18	15	9.13
PAC	5 ppm PAC	2.4	2.3	8.72
PAC	20 ppm PAC	2.9	2.9	8.70
$FeCl_3$	5 ppm $FeCl_3$	7.5	7.5	-
$FeCl_3$	20 ppm $FeCl_3$	25	26	7.77
Untreated BR48		1.7	1.7	8.76

*Turbidity measured from top portion of the jar

Ferric chloride produced light to dark yellowish brown colloidal particles even at 5 ppm dosing concentration. The water also turned yellowish brown color which is probably $Fe(OH)_3$ colloids present in solution. Calcium hydroxide did not easily dissolve in water and may interfere the turbidity giving higher values. Unfortunately, a blank turbidity check using distilled water with lime dosing was not conducted. Lime being a basic or alkaline flocculant, its addition increased the pH of the final test solutions proportional to the dosing concentration (e.g. pH 8.9 at 5 ppm Ca and 9.13 at 20 ppm Ca). This may also contribute to the effect in the aggregate formation of silica. Ferric chloride and aluminum chloride stock solutions were normally prepared in acidified solutions where they are more stable. The resulting pH of the test solutions decreased compared to the untreated water. Lower pH values were obtained with higher concentration of these flocculants.

Further tests were conducted using concentrations up to 100-300 ppm of the inorganic flocculants. This was done to determine flocculant concentration required for rapid flocculation of colloidal silica without added polymers. At the dosing concentration where silica flocculates but remains suspended, a combination with the organic polymers was also tested The dosing range is only approximate and low flocculant concentrations ranges from 5 to 100 ppm depending on the electrolyte. The term rapid sedimentation is defined as the formation of gel between 10 to 20 minutes; while stable suspension is defined at 80 to 90 minutes without decline in turbidity. For ferric chloride and plyaluminum chloride, silica immediately formed aggregates even at ≤5 ppm concentration but settling did not take place at this low concentration. Calcium chloride and magnesium chloride did not produce rapid flocculation in less than 20 minutes even up to 300 ppm. However, magnesium chloride showed an increasing turbidity at 300 ppm indicating slow aggregation as shown in Table 5 and Figure 5.

TABLE 5. EFFECT OF $MgCl_2$ and $CaCl_2$ ON TURBIDITY OF BR48 WATER

Time min.	*Turbidity (NTU)*					
	Magnesium chloride (ppm as Mg)			*Calcium chloride (ppm as Ca)*		
	100	*200*	*300*	*100*	*200*	*300*
10	2.5	2.5	3	2.5	2.5	2.5
20	2.5	2.5	4	2.5	2.5	2.5
50	2.5	2.5	7.5	2.5	2.5	2.5
60	2.5	2.5	12	2.5	2.5	2.5
90	2.5	2.5	18	2.5	2.5	2.5
110	2.5	2.5	24	2.5	2.5	2.5
130	-	-	26	-	-	2.5

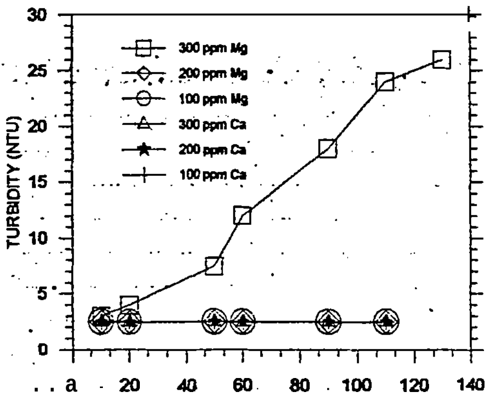

Figure 5 Effect of $CaCl_2$ and MgCl2 on turbidity of BR48 water

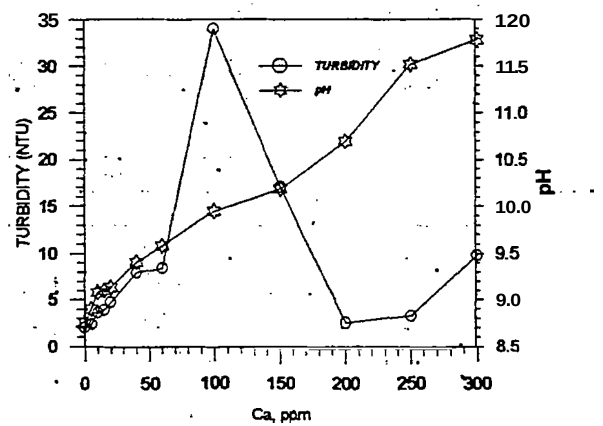

Figure 6. Effect of lime on turbidity of BR48 water

Calcium chloride was not evaluated further for having shown to be ineffective in this test. Table 6 shows the results of the performance of the inorganic flocculants in terms of minimum concentration for rapid flocculation and maximum concentration for aggregated silica to remain stable. The data were obtained over several test runs. This result may indicate that ferric chloride is the most effective flocculant since it requires the lowest concentration of only 20 ppm for rapid gel formation to occur at this temperature. However, the formation of yellowish brown $Fe(OH)_3$ colloid has contributed to the high turbidity value when ferric chloride was used Tests at lower concentration (below 1 ppm) of ferric chloride which could minimize or eliminate the effect on turbidity due to formation of $Fe(OH)_3$ were not conducted. Table 8 shows the effect on turbidity of BR 48 liquid using different concentration of ferric chloride. The turbidity of liquid increased with increasing concentration of ferric chloride for the first 5 minutes. At 40 ppm $FeCl_3$, rapid flocculation occurred which caused the precipitate to settle. Higher concentration of calcium hydroxide (>50 ppm ,Figure 6) is required to flocculate the colloidal silica.

TABLE 6. MINIMUM DOSING CONCENTRATION TO OBTAIN RAPID FLOCCULATION AND MAXIMUM CONCENTRATIONFOR A STABLE SUSPENSION

Flocculant	*Minimum Gel formation concentration*	*MaximumStable Suspension concentration*	*Turbidity (NTU) at stable suspension*
PAC	≥200 ppm as PAC	100 ppm as PAC	30
$FeCl_3$	20 ppm as $FeCl_3$	5 ppm as $FeCl_3$	7.5*
$Ca(OH)_2$	≥50 ppm as Ca	≤10 ppm as Ca	3.4
$MgCl_2$	>400 ppm as Mg	≤300 ppm as Mg	5-18

*Turbidity measurement may include $Fe(OH)_3$ colloids.

TABLE 7. EFFECT OF $Ca(OH)_2$ CONCENTRATION ON TURBIDITY OF BR 48 WATER

ppm Ca	*Turbidity (NTU)*				*Final*
	5-10 minutes		*90 minute*		*pH*
	Top	*Bottom*	*Top*	*Bottom*	
0	2	2	2	2	8.75
5	2.4	2.5	2.4	2.4	8.90
10	3.6	3.9	3.4	3.3	9.08
15	3.9	3.9	3.3	3.3	9.10
20	4.7	5.1	3.8	4.2	9.13
40	7.9	8.0	6.3	6.0	9.40
60	8.4	10.3	8.1	8.5	9.58
100	34	100	-	-	9.95
150	17	Gel	-	-	10.18
200	2.5	Gel	-	-	10.69
250	3.3	Gel	-	-	11.52
300	9.8	Gel	-	-	11.78

Gel - precipitate has settled

TABLE 8 EFFECT OF $FeCl_3$ CONCENTRATION ON TURBIDITY OF BR 48 WATER

ppm $FeCl_3$	*Turbidity (NTU)*				*pH*
	5 minutes		*20 minutes*		
	Top	*Bottom*	*Top*	*Bottom*	
0	2.8	2.8	-	-	8.8
5	7.5	7.5	7.5	7.5	-
10	14	14	14	14	-
20	25	25	26	gel	7.77
40	53	54	20	gel	6.92

3.2.3 *Combination of* Inorganic *Flocculants* with *Polymer flocculants*

Inorganic flocculants, where rapid flocculation is relatively slow (>120 minutes settling time) were combined with anionic and nonionic polymer flocculants to *study* their effect on settling rate when there is already sufficient aggregated silica. Polyaluminum chloride at 100 ppm concentration was used since this produces high turbidity and the aggregated silica suspension remained stable for almost two hours. The anionic and nonionic polymers were found to have no effect when used alone in earlier tests. The results of combined inorganic and organic polymer flocculant will provide some understanding on applications related to the control of silica particle *size.* This test will also evaluate the effect of differences in anionic charge to the flocculation rate in the presence of trivalent ions like aluminum. Magnesium was also tested in combination with the anionic and nonionic flocculants since its effect in flocculation when used alone at lower concentration (<300 ppm) is relatively slow. It was thought that divalent cations like magnesium chloride will serve as links and promote adsorption of the nonionic polyacrylamide flocculants by ionic bonding to promote bridging of the polymers with silica particle. Combination of magnesium chloride with the polymer flocculants will therefore determine this adsorption and effects. In experiments requiring controlled particle size of silica particle, the method involve initial addition of cationic electrolytes (such as Ca^{+2}, Mg^{+2}, Al^{+3}) to agglomerate or coagulate the polymerized silica particles followed by flocculants and dispersing agents to separate and remove silica. The inorganic and polymer flocculant combination will *test this* particular aspect with the effect in flocculation rate.

In these tests, silica particles is initially agglomerated using polyaluminum chloride (PAC) or magnesium chloride followed by flocculation using the polymer flocculants. Turbidity was determined before and after addition of flocculants and monitored with time thereafter. The result of these tests are shown in Figures 7 and 8 and Tables 9 and 10.

TABLE 9. EFFECT OF PAC AND POLYMER FLOCCULANTS ON TURBIDITY OF BR 48 WATER

Time	*Turbidity (NTU)*					
min.	*ME24*	*M 156*	*M1011*	*M 155*	*M 919*	*M 351*
5	3	3	3	3	3	3
12	30	30	30.5	30.5	30	30
20	30	30	30.5	30.5	30	30
40	30	11.5	15	30	9	30
80	30	11.5	14.5	28.5	8.5	30
100	30	11.5	14	28.	8	30

Notes :pH untreated = 8.4 pH with 100 ppm PAC = 7.6 M - Magnafloc

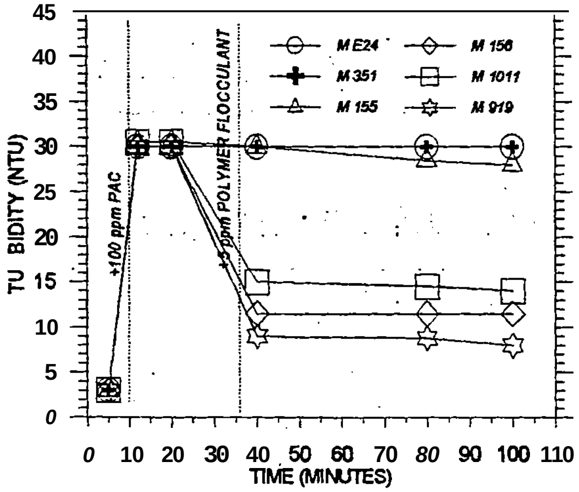

Figure 7. Effect of PAC with *added polymer flocculants on turbidity of BR 48 water*

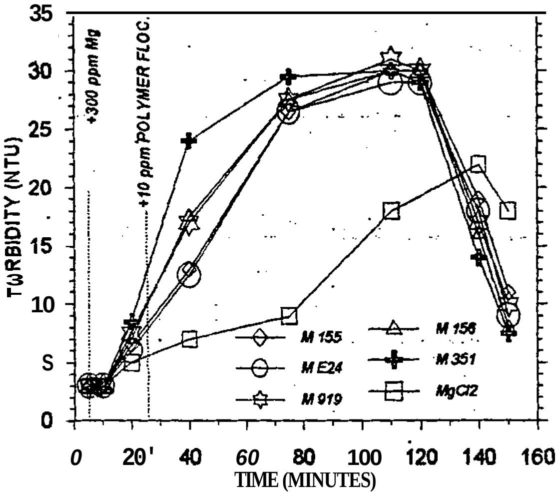

Figure 8. Effect of $MgCl_2$ with added polymer flocculants on turbidity of BR 48 water

The results showed no change in turbidity of the suspension using M 351 (a non-ionic flocculant) and M E24 the least anionic charged flocculant. Only a minor drop in turbidity was observed with M 155. The other anionic flocculants increased the flocculation rate as shown by a drop in turbidity of the suspension. Further addition of 5 ppm flocculants (total of 10 ppm) did not change the turbidity of the suspension indicating that the flocculant could be used at concentration lower than 5 ppm. The order of decreasing effect on the flocculation or settling of the colloidal silica are as follows: M 919 > M156 > M 1011 > M 153 > M E24, M 351. The decreasing effect of flocculation on colloidal silica by the above flocculants correlated with their decreasing ionic character where: M 919 > M 156 > M 1011 > M 155 > M E23.

For the test conducted using magnesium chloride in combination with the anionic flocculants (Figure 8, Table 10), a simultaneous run using purely magnesium chloride at 300 ppm was conducted to help evaluate the changes in turbidity of untreated solution. The test run was conducted for a longer period than that with polyaluminum chloride (150 minutes) and the flocculant dosage was increased to 10 ppm compared to 5 ppm using PAC. The results showed an increase in turbidity with time for all test solutions including pure magnesium chloride up to about 110 minutes then a decrease in turbidity after this period (Figure 8). Higher turbidity is observed in test solutions with addition of synthetic polymer flocculants. There is no significant difference between the anionic polymers and they have similar *effect* in terms of their enhancement in flocculation when combined with magnesium. The result also showed a slower flocculation rate (120 minutes to obtain maximum turbidity and 20 minutes to start settling) compared to polyaluminum chloride combination indicating a slightly different flocculation process. The gradual increasing turbidity could be a manifestation of the ion binding adsorption mechanism where the divalent magnesium ions will bind strongly with the carboxylate group of the polyacrylamide and will also serve to link these groups to the negative sites of the silica particle. The Mg^{+2} ion will also bind to the silica colloid and change the surface charge of the colloid This type of bonding is not observed between PAC with added nonionic polymer.

TABLE 10. EFFECT OF $MgCl_2$ WITH ADDED POLYMER ON TURBIDITY

Time	*Turbidity (NTU)*					
min.	*+M E24*	*+M 155*	*+M 156*	*+M 919*	*+M 351*	*$MgCl_2$*
5	3	3	3	3	3	3
10	3	3	3	3	3	3
20	6.0	6.5	7.0	7.5	8.5	5
40	12.5	13	17.5	17.0	24	7
75	26.5	26.5	27.5	27.5	29.5	9
110	29.0	30	30	31	30	18
120	29.0	30	30	30	29	-
140	18	19	16	17	14	22

***Source** : Top portion of Jar*

The effect of 100 ppm polyaluminum chloride and 200 ppm magnesium chloride with added cationic and anionic polymers were compared and run simultaneously. The nonionic flocculant and other cationic flocculant were tested later as shown in Table 13. The concentration of magnesium chloride was lowered down to 200 ppm as compared to the previous test of 300 ppm. This is to test further the effect of anionic flocculant at lower magnesium chloride concentration. A concentration of 5 ppm was used for the flocculant. Zetag 45 has the lowest cationic charge character of the cationic group and M 919 has the highest anionic character of the anionic group. These combinations will represent an extreme situation for $MgCl_2$ -anionic case of lower flocculation effect and the best flocculation enhancement for PAC-anionic combination. It was observed in the previous test using 300 ppm Mg that the nonionic flocculant has a slightly higher flocculation rate compared to anionic.

During the test, a 2-3 minutes stirring time between addition was made after which the particle suspension was allowed to settle and the turbidity was measured with time. The results is shown in Table 11 and plotted in Figure 9. The result with magnesium chloride showed an enhancement in turbidity using cationic charge flocculant (Z 45) but with a decreasing turbidity nith time which indicate flocculation of the particles. There is no turbidity change with the highly anionic charge flocculants (M919) when combined nith MgCl2. For the PAC test solutions, there is rapid drop in turbidity (5 minutes) for both-cationic (Z 45) and anionic polymer. There is only a gradual decline in turbidity when using PAC alone. This indicates an increase in settling rate of the silica colloids when combined with PAC and ionic flocculants. A slightly lower turbidity was observed with PAC and M 919 combination compared to Z 45 and PAC indicating more enhance flocculation using M 919.

TABLE 11. EFFECT OF $MgCl_2$ AND PAC WITH ADDED POLYMER FLOCCULANT ON TURBIDITY

Polyelectrolyte concentration.		*Turbidity (NTU)*				*pH*
		5min.	*10min.*	*60min.*	*85min*	
200 ppm Mg	none	3.1	3.1	3.1	3.1	8.5
200 ppm Mg	5 ppm Z 45	16	15	10	6	8.5
200 ppm Mg	5 ppm M919	3.2	3.1	3	3.3	8.5
100 ppm PAC	none	30	29	25	25	7.8
100 ppm PAC	5 ppm Z 45	30	9	8	8	7.8
100 ppm PAC	5 ppm M 919	30	5	5	5	7.8

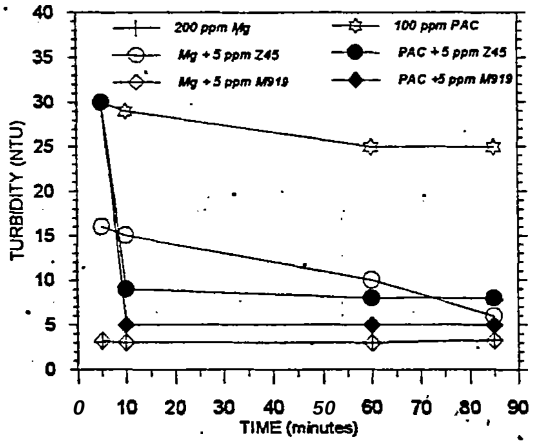

Figure 9. Effect of MgCl2 and PAC with added cationic and anionic polymer flocculant on turbidity of BR48 water

When PAC was combined with higher cationic charge (compared to Z45) such as Z 63 and Z57 (Table 12), there was no observed decline in turbidity even up to 40 minutes but a slight increase (1 NTU) .This will indicate the effect of decreasing the settling rate of PAC when added with increasing cationic charge polymers. The settling period (40 minutes) may not also be sufficient for settling to occur. This observation could also be a manifestation of colloidal stabilization by repulsive action due to the presence of a large quantities of the trivalent aluminum ions against the cationic charged polymer flocculant. The colloids formed by the addition of polyaluminum chloride could be in the form of $Al(OH)_3$ during this stage which is stable in the presence of cationic polymer. Generally, the combination of PAC with polymer flocculants of higher of cationic charge such as Z 63 and Z57 will not give good results in terms of attaining rapid flocculation of silica particle.

TABLE 12. EFFECT OF PAC WITH ADDED POLYMER FLOCCULANTS ON TURBIDITY OF BR 48

		Turbidity (NTU)			
Solution A	*Solution B*	*A only*	*Solution A + B*		
		0 min	*5 min*	*20 min*	*40 min*
none	5 ppm Z 57	2	5	5	5
100 ppm PAC	5 ppm Z57	25	28	27	27
none	5 ppm Z63	2	7	7	7
100 ppm PAC	5 ppm Z63	26	27	27	27
none	5 ppm M1101	2	2	2	2
100 ppm PAC	5 ppm M1011	26	15	14	14
100 ppm PAC	none	24	22.5		23
100 ppm PAC	5 ppm M 351	24	22.5		23

4.0 SUMMARY AND CONCLUSIONS

4.1 Performance of individual flocculants on turbidity

Cationic polymers

The cationic polymer flocculants (Zetag) tested produces rapid agglomeration of silica but the flocculant also formed a long gelatinous. niucus-like, sticky precipitate when added to the geothermal **liquid** The occurrence of this precipitate is partly attributed to the poor dispersion technique used in the jar test experiment and the **high** concenration of stock solutions used (0.1 %).The effect on turbidity of the cationic polymer flocculants is correlated to their increasing cationic charge which enhances agglomeration of silica. There was no enhancement in flocculation or settling rate with these polymers which could be due to the "sweep flocculation" mechanism which is an irreversible process that produces relatively small agglomerated particles. The decreasing effect on turbidity is as follows: Z 63 > Z 57 > Z92 > Z45.

Anionic and nonionic polymers

The anionic and nonionic charged flocculants composed of the Magnafloc series did not induce flocculation when used alone.

Inorganic electrolytes

The inorganic flocculants (polyaluminum chloride. ferric chloride and calcium hydroxide) 'increase the agglomeration of silica particles even at concentrations of 5-20 ppm. Higher concentrations of these flocculants are required for rapid flocculation to occur. Fomiation of the hydroxide colloid of iron and aluminum at high dosing concentrations could also affect the flocculation and turbidity measurement. Magnesium chloride requires greater than 300 ppm to increase the rate of flocculation. There was no observed flocculation using calcium chloride up to 300 ppm. The order of decreasing effect on flocculation rate of silica is as follows: $FeCl_3 > Ca(OH)_2 > PAC > MgCl_2 > CaCl_2$

4.2 Combination of organic polymers with inorganic flocculants

Combination with magnesium chloride

The presence of divalent cations such as magnesium increased the flocculation rate when combined with the anionic and nonionic flocculants. The enhancement in flocculation of the nonionic and anionic flocculants nith magnesium chloride is due to ionic bonding between magnesium ions **and** the carboxylate group of the acrylamide which will change the surface charge of the particle and promote attraction by bridging processes. The increasing effect of the anionic polymers is correlated to their decreasing aniomc charge (e.g. smaller anionic charge increases the flocculation rate) with the nonionic having the highest effect on flocculation. The loner cationic charge polymers have higher flocculation rate when combined with magnesium.

Combination with polyaluminum chloride

The anionic polymers increase the flocculation rate when combined with polyaluminum chloride. The increasing effect in flocculation is correlated to the increasing aniomc charge of the polymer which is opposite to the effect with magnesium chloride combination. The cationic charge character of the polymer decreases the flocculation rate when combined nith polyaluminum chloride - highly cationic have the lowest effect in flocculation rate similar to the effect with $MgCl_2$ combination. The nonionic polymer nith polyaluminum chloride did not enhance flocculation. The enhancement in flocculation of the anionic polymers could be a charge neutralization process where the silica particle is first agglomerated by the addition of polyaluminum chloride and this changes the surface charge of the silica particle. The addition of anionic charge polymer resulted in another change in surface charge of the agglomerated particles and promote particle bridging and flocculation. The above process is different from magnesium chloride since there are no agglomerated particles initially formed by magnesium chloride. The cationic polymers have similar effects in terms of decreasing flocculation rate with increasing ionic charge when combined with magnesium or polyaluminum chloride.

The above results will provide preliminary information on the types of flocculants or polymers to be used in applications related to the control of silica scaling deposition, particle size of silica and colloidal silica stabilization.

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