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Coagulation Chemistries for Silica Removal from Cooling Tower Water

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ABSTRACT

The formation of silica scale is a problem for thermoelectric power generating facilities, and this study investigated the potential for removal of silica by means of chemical coagulation from source water before it is subjected to mineral concentration in cooling towers. In Phase I, a screening of many typical as well as novel coagulants was carried out using concentrated cooling tower water, with and without flocculation aids, at concentrations typical for water purification with limited results. In Phase II, it was decided that treatment of source or make up water was more appropriate, and that higher dosing with coagulants delivered promising results. In fact, the less exotic coagulants proved to be more efficacious for reasons not yet fully determined. Some analysis was made of the molecular nature of the precipitated floc, which may aid in process improvements. In Phase III, more detailed study of process conditions for aluminum chloride coagulation was undertaken. Lime-soda water softening and the precipitation of magnesium hydroxide were shown to be too limited in terms of effectiveness, speed, and energy consumption to be considered further for the present application. In Phase IV, sodium aluminate emerged as an effective coagulant for silica, and the most attractive of those tested to date because of its availability, ease of use, and low requirement for additional chemicals. Some process optimization was performed for coagulant concentration and operational pH. It is concluded that silica coagulation with simple aluminum-based agents is effective, simple, and compatible with other industrial processes.

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1 INTRODUCTION

The threat of silica (SiO_2) scale formation on internal surfaces of heat-exchanging equipment has plagued industry at least since the advent of high pressure steam systems in the 1930s. It has increasingly concerned designers and operators of thermoelectric generating plants as demands for more efficient use of scarce water resources have prompted a shift from once-through systems to the recirculation of water through cooling towers with their inevitably rapid concentration of minerals. Once scaling occurs, cleaning is a costly recourse, involving down time and hazardous waste generation. While scale inhibition using newer, more expensive additives shows promise, typical polyphosphate and phosphonate antiscalants are ineffective against silica deposition, leaving frequent blowdowns as the only readily available and effective remedy. Reverse osmosis (RO) and nanofiltration (NF) technologies offer the prospect of ancillary control of dissolved solids. Yet the water purification and desalination industries themselves face a common challenge, with filtration membranes being especially sensitive to fouling with silica.

The study presented in this report has extensively investigated the chemistry of coagulation as a preventive approach, with an eye toward removing silica from tower water or make up water at the front end to greatly delay supersaturation. Most inorganic, organic and microbiological contaminants in water at $\text{pH} > 7$ carry a negative charge, as do dissolved silica ions. Thus, the initial water treatment process in a municipal plant is the addition of a cationic coagulant. The cationic coagulant functions simply by neutralizing the anionic contaminants, and the neutralized mass aggregates and precipitates as an easily separated "floc". Typical coagulants include ferric and aluminum salts, as well as cationic polymers or surfactants. Co-coagulants are hydrophobic anionic polymers or surfactants that aid in rapid aggregation, and magnesium, calcium, or other polyvalent cations can be effective co-coagulants as well. In theory, the presence of silica may be ameliorated with the proper application of this well-known technology.

1.1 Background and Objective

In 1940, a review of the silica problem by Behrman and Gustafson^[1] described the state-of-the-art solution to SiO_2 removal from industrial water as consisting of a soda-lime [Na_2CO_3 and $\text{Ca}(\text{OH})_2$] water softening procedure combined with coagulation using ferric sulfate [$\text{Fe}(\text{SO}_4)_3$]. The treatment method was considered successful with the finished water containing more than 180 ppm of new dissolved solids and a residual SiO_2 of close to 15 ppm. Since that time, little has changed in the way this issue is handled. Most progress has occurred in comprehensive water purification for municipal use. Therefore, as advances have arrived in removal of infectious agents, dissolved organic compounds and other contaminants from drinking water, little attention has been given to silica because its consumption is not considered hazardous to humans.

With water shortages prevalent in many parts of the world and looming in others, it has been desalination engineers and other users of RO who are revisiting the critical question of silica scaling. Yet once again, reliance is falling on municipal-type purification systems. More

contemporary investigations from this field^[2] continue to report that soda-lime softening is sufficient for reducing silica to manageable concentrations, and that additional steps, such as coagulation, appear to be superfluous. There are several caveats. First is that for chemical softening to be effective in collaterally reducing silica, “hot” softening is needed ($>100^{\circ}\text{C}$) in a containment system over hours or even days. “Warm” softening at $70\text{-}100^{\circ}\text{C}$ is less effective^[3], and an ambient process provides no reduction at all.

It has been known for many years that silica removal during soda-lime softening is dependent on the precipitation of dissolved magnesium present in water by its conversion to $\text{Mg}(\text{OH})_2$ at a pH above 10.2. Concentrated sodium hydroxide is needed to reach the necessary alkalinity. Indeed, Al-Rehali^[3] recommends using NaOH as a single agent to replace soda and lime in removing silica. But the magnesium content native to raw water is variable and often insufficient, necessitating analysis and supplemental dosing with magnesium compounds.

These observations are informative but not directly applicable to single-point users of water, such as electric generating stations, in which the benefits of comprehensive softening and purification are neither appreciable nor affordable. The object of the present investigation is a greater understanding of chemical coagulation of silica, building toward an alternative, well-focused method of silica removal that could be integrated into a thermoelectric system with a small footprint and potentially to be synergistic with other measures employed.

1.2 Criteria for Suitable Coagulation Chemistries

To be considered as a reasonable component of silica control for prevention of scaling, a chemical coagulation system must meet the following needs:

- Require the minimum number and volume of additional chemical agents to be inventoried and handled
- Minimize the use of hazardous chemicals and generation of hazardous wastes
- The process is rapid enough to match the necessary intake of make up water
- A flocculent precipitate containing silica is easily removed from the system by settling and/or simple filtration
- Able to be installed in-line with a small spatial footprint and energy demand
- Result in a processed water with silica reduced by at least 80% and at a pH compatible with other components and processes or discharge

1.3 Approach of the Study

The approach of this study was direct: to identify and optimize coagulants for silica precipitation. This was done by testing a typical suite of coagulation reagents such as alum (aluminum sulfate), ferric chloride and prehydrolyzed aluminum salts. Prior to this study, we investigated derivatives of pre-hydrolyzed aluminum salts^[4]. These salts contain a mixture of polyaluminum cations that are deemed the active ingredients and were found to be effective in flocculating other anionic contaminants. Therefore, these and other novel coagulants were included.

In addition, some attention was given to surfactants and other flocculation aids which have been commercially employed in or proposed for water purification. In small amounts, these can benefit in enabling the more economical use of primary coagulant chemicals.

The first phase of study involved the screening of the wide array of potential agents, using them at customary concentrations in water sampled from cooling towers at Sandia National Laboratories in Albuquerque, NM, known to have silica at or near saturation levels. This was to be a sensitive measure of the agents' relative potentials to precipitate the silica.

With several candidates identified, the study moved on to the treatment of unconcentrated source water, which would be a more reasonable target in any upscaled practice but provides a greater challenge to coagulation. This phase also provided floc material (settled solids) for chemical analysis. The silica-depleted water was also analyzed for its other contents, such as residual aluminum. As the findings themselves led to a greater understanding of the principles involved with silica coagulation, experiments were fine-tuned to yield information necessary for final recommendations.

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2 EXPERIMENTAL

2.1 Overview

The work described in this report was performed in four phases:

In **Phase I** an initial screening was conducted that examined the use of aluminum, iron and molybdenum based Keggin-ion coagulants

In **Phase II** some of the same coagulants tested in Phase I were examined, but at higher concentrations of the coagulants with and without the addition of surfactants and magnesium supplementation. While in Phase I, pH adjustments had been made only after dosing with coagulant, the pH of test waters was manipulated in some Phase II experiments to theoretically solubilize the silica for greater availability to the coagulation process. Emphasis was placed on the polyaluminum chloride products produced by Kemira Water Solutions, Inc. In this phase, solid-state MAS NMR (magic angle spinning nuclear magnetic resonance) was used to characterize the alumina-silica flocs.

In **Phase III** a suite of experiments was run to examine alternatives to the coagulants tested in Phases I and II and provide supportive data. These experiments include: 1) examination of aluminum chloride (AlCl_3) as a less expensive, more commonplace alternative to PAX-18, 2) alumina-precipitated flocs were analyzed to determine what elements they contained in addition to silicon and aluminum, 3) the role of magnesium in silica removal, with and without AlCl_3 , was studied, and 4) a test was run to compare results of AlCl_3 -mediated coagulation with soda-lime water softening methods, sometimes proposed as a suitable silica removal strategy.

In **Phase IV**, sodium aluminate (NaAlO_2), was tested as a readily available, readily soluble aluminum-based coagulant with the prospect of efficacy without the need for extreme pH adjustment. A process using this chemical was characterized for optimal pH and dose ranging.

Below is an overview of materials and methods used in the experimental work. More detailed descriptions of methods specific to the different phases are also included in Section 3.

2.2 Materials

Water for early treatment experiments was drawn from either of two cooling towers in use at Sandia National Laboratories (SNL) buildings 823 and 897 (typically pH 8.4 - 9.00, conductivity 1390 - 1580 $\mu\text{S}/\text{cm}$, SiO_2 126 - 177 ppm). The cooling tower water was used in the first series of experiments to quantify a greater range of effectiveness and because its high concentration of silica would be sensitive to precipitation. In follow-up studies, the tap water (typically pH 7.9 - 8.5, conductivity 362 - 374, 32 - 35 ppm SiO_2 , alkalinity 88 ppm) at Kirtland Air Force Base was characterized and used for a given series of experiments on a set of coagulants. This is minimally treated (chlorinated only) ground water, also used as make up water for SNL cooling towers, mentioned above, and typical of groundwater in the Western United States. The

polyaluminum Keggin ion coagulants Al_{13} , GaAl_{12} , BAl_{12} and GeAl_{12} were synthesized as solutions by alkaline hydrolysis^[7]. The solutions were either used directly (referred to as crude solutions, see Table 1), or crystallized as a selenate salt and redissolved (referred to as metathesized, see Tables 1 and 2). Polyaluminum chloride products (PAX10, PAX14, PAX-XL19, PAX-18) were provided by Kemira Water Solutions, Inc. The anionic surfactant used was sodium dodecyl sulfate (SDS) prepared as a 1% concentrate, and the cationic surfactant was cetyltrimethylammonium chloride (c-TMACl) (Aldrich, 25% solution). Ferric chloride, aluminum sulfate and other reagents were also purchased from Aldrich. IWE-830, an anionic, polymeric flocculation aid was obtained from Industrial Water Engineering, Albuquerque.

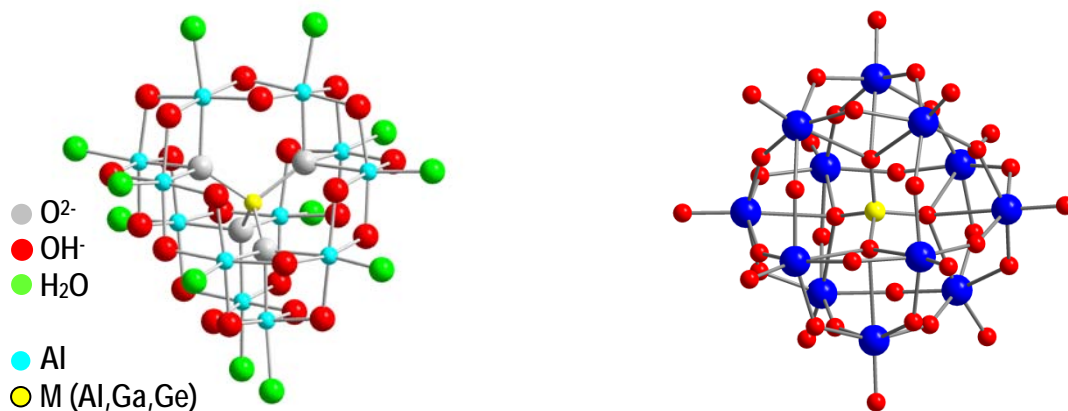


Figure 1. Polycationic Keggin ions

Left: Aluminum polycation Keggin ion, $[\text{MO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7.8+}$ ($\text{M}=\text{Al}, \text{Ga}, \text{Ge}$): Al_{13} , GaAl_{12} , GeAl_{12} .
Right: $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ Keggin ion, SiMo_{12} . Blue=Mo; yellow=Si; red=O.

2.3 Methods

Determination of silica concentrations in solution before and after coagulation experiments was carried out using the Hach[®] high range silicomolybdate method, which is accurate between 1 and 100 mg/L. If dilution was required to bring samples into this range, it was by the addition of water certified to be silica-free. Briefly, Na_2MoO_4 is dissolved in a 10-mL sample and solid sulfamic acid is added, causing a yellow complex to develop for ten minutes. Interference by phosphates is eliminated by adding citric acid, and absorbance at 420 nm is read to measure the concentration of silica as silicomolybdate. The precision and reproducibility of this assay was validated before its use in the study.

Coagulation experiments were performed at room temperature, typically with 100 to 1000 mL of water in multiple glass beakers. Once coagulants were identified for their potential, volumes as small as 10 mL were treated in multiple screw-capped tubes in order to subject water to varied conditions simultaneously. If magnesium was added (as MgSO_4), it was dissolved in the raw water ahead of time. Coagulants were added as specified amounts of concentrates to the tubes, increasing the test volumes by no more than 5%, and mixed in quickly by magnetic stirring or capping the tubes and inverting them twice. Depending on the experiment, pH of the water was adjusted with NaOH or HCl either before coagulation, immediately after, or not at all. The final pH of each mixture was measured and samples were placed on a rocker or slowly stirred (60

rpm) for gentle agitation during the flocculation period. If a surfactant was employed, it was added after the first five minutes of flocculation. The density, volume and settling of the floc was observed after 15 minutes of development and it was separated from treated water by centrifugation at 2000 rcf (relative centrifugal force).

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3 RESULTS AND DISCUSSION

Phase I. Initial Screening

The choice of experimental conditions was not as straightforward as the textbook use of coagulants for water purification. The familiar cationic coagulating agents are usually most effective in the acidic ranges of the pH scale^[5], typically pH 5 to 6.5, and most are insoluble at or above neutrality. While there are a few references to removal of silica in the neighborhood of pH 5 - 6 using ferric coagulants, the solubility of silica is at a low point between pH 7 and 8, where its precipitation would seem likelier. At the same time, it is known to co-precipitate with MgOH under extremely alkaline conditions, for reasons that are incompletely understood^[6]. Therefore, the screening of a potential coagulant was conducted at several pH points, often at one where it was known to be effective against turbidity, for example, and another at the native pH of the water or a pH (7 - 8) informed by knowledge of silica's solubility range.

Coagulant dosing was standardized in terms of the active metal constituent. For instance, AlCl_3 contains a different proportion of aluminum than does $\text{Al}_2(\text{SO}_4)_3$, but they were used at concentrations normalized to aluminum mg/L (ppm). Two series of experiments were conducted to test the efficacy of aluminum and iron-based coagulants (Tables 1 and 2). The first set of experiments (Phase I) tested low concentrations of coagulants (20 ppm of the metal, Al and Fe). This concentration of the inorganic (metal) coagulant was initially investigated since it is sufficient for removal of other anionic contaminants such as clays, bacteria, natural organic material and viruses^[7]. The relative concentrations of Al/Fe to Si in these studies are approximately 1:4. Selected results from this phase are presented in Table 1.

Table 1
Summary of Phase I SiO₂* Precipitation from Cooling Tower Water
(Highlighted in bold red are the most successful experiments)

Coagulant	ppm metal of coagulant	final pH [‡]	Co-coagulant	% SiO ₂ Removal
GaAl ₁₂ ^a -M ¹	20	8.6		13
Al ₁₃ ^b -C ²	20	8.6		7
PAX19 ⁴	20	8.7		18
GaAl₁₂-M¹	20	7.1		27
Al₂(SO₄)₃	20	7.1		27
GaAl ₁₂ ^a -M ¹	20	7.1	IWE830 ⁵ 1 ppm	24
Al ₁₃ ^b -C ²	20	7.1	colloidal clay ³	13
PAX19 ⁴	20	7.1	colloidal clay	18
GaAl ₁₂ ^a -M ¹	20	7.1	colloidal clay	15
FeCl ₃	20	6.0		0
FeCl ₃	20	6.0	c-TMACl ⁶ 13 ppm	0
GeAl ₁₂ ^c -M ¹	20	8.6	SDS ⁷ 50 ppm	21
GeAl ₁₂ ^c -M ¹	20	6.3	SDS ⁷ 50 ppm	20
Na₂MoO₄	3500	3.5	c-TMACl⁶ 90 ppm	95

*Initial SiO₂ concentration is 177 ppm and pH=9.0.

[‡]pH is primarily a function of initial adjustment.

^aGa-centered Keggin ion [GaO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁺

^bAl-centered Keggin ion [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁺

^cGe-centered Keggin ion [GeO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁸⁺

¹M=metathesis (purified) preparation—see text.

²C=crude preparation—see text

³Clay suspension added to provide about 20 NTU of turbidity.

⁴Polyaluminum chloride (PACl) formulation manufactured by Kemira; pH=4.34.

⁵Anionic polymer manufactured by International Water Engineering, Albq NM.

⁶Cationic surfactant; cetyltrimethylammonium chloride

⁷Anionic surfactant; sodium dodecylsulfate

None of the coagulants achieved impressive removal of silica under the conditions of these trials, although GaAl₁₂ and Al₂(SO₄)₃ made a fair showing at pH 7.1, without any additional additives. Colloidal clay particles are known to provide additional surface area for precipitation of certain impurities, but were of no benefit here. Ferric chloride, within its customary operating range at pH 6.0, had no effect on silica and was dropped from further consideration during experiments on cooling tower water.

In addition to the aluminum and iron-based coagulants, SiMo_{12} Keggin ions were tested as a potential silica coagulant. It was known that the Hach[®] assays for silica concentration form the SiMo_{12} Keggin ion (see Figure 1), which is yellow when fully oxidized (for high Si concentration assays), and blue when reduced (for low concentration assays). Since the silica is sequestered in the center of SiMo_{12} , we investigated precipitation with the cationic surfactant, c-TMACl. An experiment with a Si:Mo ratio of 1:12.8 was performed first (Phase I, Table 1) and an experiment with Si:Mo ratio of 1:4.7 was run as part of the Phase II experiments (Table 2).

Table 2
Summary of **Phase II** SiO_2^* precipitation from Cooling Tower Water

Coagulant	ppm metal of coagulant	final pH [*]	Co-coagulant	% SiO_2 Removal	pH adjustment prior to coagulant addition
$\text{GaAl}_{12}^{\text{a}} - \text{M}^1$	80	7.2	Bis-Tris buffer for pH	55%	
$\text{GaAl}_{12}^{\text{a}} - \text{M}_1$	80		Polyacrylamide	20%	
PAX10 ⁴	80	3.5	citric acid for pH	0	
PAX10	80	8.7	c-TMACl ² 125 ppm	45%	
PAX10	178	6.6	c-TMACl ² 63 ppm	40%	
PAX10	178	6.6	SDS ³ 100 ppm	45%	
PAX10	178	6.6		42%	
Na_2MoO_4	1280	3.25	c-TMACl ² 63 ppm	7%	
PAX10	178	6.6	SDS ³ 50 ppm	56%	
PAX10	178	6.0	SDS ³ 50 ppm	35%	7.0
PAX18 ⁵	128	5.5	9 mM Mg, SDS ³ 50 ppm	51%	
PAX18	128	6.1	9 mM Mg, SDS ³ 50 ppm	58%	9.3
PAX18	128	7.0	9 mM Mg, SDS ³ 50 ppm	71%	9.6
PAX18	178	5.9	9 mM Mg	45%	
PAX18	178	6.1	9 mM Mg	55%	9.2
PAX18	178	6.5	9 mM Mg	62%	9.6
MgSO_4	217	8.96	9 mM Mg (alone, no Al)	6%	
PAX18	178	7.0	9 mM Mg	75%	1 hr at 9.5
PAX18	178	7.0	9 mM Mg, SDS 50 ppm	74%	1 hr at 9.5
PAX18	178	7.0		81%	1 hr at 9.5
PAX18	178	7.0	c-TMACl² 125 ppm	80%	1 hr at 9.5

*Initial SiO_2 concentration is 177 ppm and pH=9.0.

^y pH is affected by added coagulant.

^aGa-centered Keggin ion $[\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$

¹M=metathesis (purified) preparation—see text.

²Cationic surfactant; cetyltrimethylammonium chloride

³Anionic surfactant; sodium dodecylsulfate

⁴Polyaluminum chloride (PACl), Kemira; pH=2.02

⁵Polyaluminum chloride (PACl), Kemira; pH=0.87

Note: the series of results for PAX18 demonstrate that neither surfactants nor magnesium aid silica coagulation.

Phase II. Higher Coagulant Concentrations Investigated

The molybdate coagulant was remarkably successful, removing 95% of silica, in the Phase I experiment at the ideal molar ratio of 1:12.8, the ratio expected in the resulting precipitate (Table 1). This outcome spurred interest in trying the Phase II series at higher concentrations of aluminum-based coagulants, while rerunning Na_2MoO_4 at a more economical concentration. The molybdate method had been reported once before in the literature for the purpose of recovering expensive silica isotopes^[8]. Its efficacy, giving 95% silica removal in the first experiment, was an incentive to continue to explore its use. Furthermore, the SiMo_{12} Keggin ion does not have complex acid-base behavior like the aluminum polycations. Therefore, if the pH is controlled (acidic), its behavior is much more predictable under variable water conditions than the aluminum coagulants. Unfortunately, the attempted silicomolybdate Keggin formation at the Si:Mo ratio of 1:4.7 was disappointing, and no further effort was made into using Na_2MoO_4 since it was required in such great amounts.

Polyaluminum chloride (PACL), particularly the PAX 18 product, provided excellent removal (approximately 80%) when used at an aluminum concentration matching that of the silica. This performance, at the end of a series of experiments using PAX 18 under different conditions, was instructive in showing that pH and aluminum dose were the overriding factors and that magnesium and surfactants were either of neutral or slightly inhibitory effect in this context.

During Phase II, results from a given coagulant were compared with and without the addition of surfactants and/or magnesium supplementation. While in Phase I, pH adjustments had been made only after dosing with coagulant, the pH of test waters was manipulated in some Phase II experiments to theoretically solubilize the silica for greater availability to the coagulation process. Emphasis was placed on the polyaluminum chloride products produced by Kemira.

Comparative study of aluminum coagulants. Since starting concentrations of silica varied and greatly affected results expressed as percent removal of silica, a head-to-head comparison of coagulants was ultimately based on removal efficiency. Removal efficiency is defined as the quotient of the amount of SiO_2 removed from solution over the amount of coagulant (ppm Al) used in treatment. A series of results are summarized in Table 3. These studies used tap water with an initial Si concentration of 30-36 ppm, and coagulant concentrations standardized at 72 ppm Al.

In prior studies on coagulation of nanometer-to-micron sized contaminants (i.e. viruses, bacteria, clay particles)^[7], we

Alumina-based coagulants efficiency
(mg SiO_2 / mg of Al used) in tap water

Coagulant	Efficiency	Best Percent Removal
PAX 18	0.43	99%
Boroalumina	0.36	70%
GeAl_{12}	0.31	69%
Al_{13}	0.24	56%
GaAl_{12}	0.22	52%

found that the more stable, less acidic Keggin ions were more effective in coagulation -- just the reverse of the hierarchy demonstrated by these determinations. The GeAl_{12} , which

Table 3

is the most acidic of the three Keggin ions previously used for general water purification, is the most efficient in silica removal. This means it is also the most reactive towards forming Al-O-Si bonds, a mechanism different from coagulation of particulates and organics.

The boroalumina coagulant (Table 3) was an experiment in synthesis as well as coagulation. We attempted to synthesize the Keggin ion with boron in the central site (yellow sphere in Figure 1) as another means of varying the reactivity of the ion towards silica precipitation. Based on our currently available data (^{27}Al NMR in the liquid state), we do not have enough conclusive evidence as to where the boron resides in the cluster, or the role it plays in coagulation. However, it clearly does have an effect, in that it performs better than GeAl_{12} , Al_{13} or GaAl_{12} .

The substance best able to remove silica in this phase of the project was the Kemira product, PAX18. Although its efficiency quotient is only modestly better than the other aluminum coagulants, that difference results in excellent clean-up in the Phase II standardized loading of 2 Al:1 SiO_2 . PAX18 is extremely acidic with a pH of 0.87, and requires considerable NaOH titration of the water to end at a pH suitable for silica flocculation. The ^{27}Al NMR analysis of PAX18 suggests it contains a range of aluminum polycations including a high concentration of the monomer, Al_{13} , as well as larger oligomers. The formulation of this coagulant is proprietary.

Finally, pH optimization was investigated for the promising alumina coagulants. In all cases, a pH of 8.0 to 8.1 enabled better SiO_2 removal than did other pH conditions during treatment. This agrees with other researchers like Brace and Matijevic^[9] who found that precipitated aluminosilicates are stabilized in this range. Table 4 gives an example using the GeAl_{12} alumina coagulant at 72 ppm.

Table 4
Silica removal from tap water as a function of pH using GeAl_{12} coagulant.

Condition	SiO_2 ppm	Percent Removed	Efficiency (ppm Si removed/ ppm Al in coagulant)
Untreated	32	-	-
pH 6.8	26.3	18%	0.08
pH 7.1	22.4	30%	0.13
pH 8.0	9.9	69%	0.30

Note: Efficient silica removal demands a pH much higher than that routinely used in removal of dissolved organic compounds, turbidity, etc. with the same coagulant.

NMR Characterization of alumina-silica flocs. By solid-state MAS NMR (magic angle spinning nuclear magnetic resonance) spectroscopy, we are able to probe the coordination of the NMR active nuclei in the solid floc formed by alumina plus silica from cooling tower. The ^{27}Al NMR spectrum of a floc formed by an approximately 3:1 Al:Si ratio is shown in Figure 2a, the CP-MAS (cross polarization) ^{29}Si spectrum is shown in Figure 2b and the direct ^{29}Si spectrum is shown in Figure 2c. The peak positions and integrations (relative intensities) are summarized in Table 5. The ^{27}Al chemical shifts and relative integration are similar to those of the pristine Al_{13} Keggin ion before reaction with silica; suggesting the Keggin ion remains largely intact upon reaction with silica. The peak at 66.7 ppm is the central tetrahedral Al (see Figure 1) and the peak at 13.3 ppm is the octahedral peak. In the Keggin ion, they are present in a 1:12 ratio; and in this floc, they are present in a approximately 1:6 ratio. This suggests that approximately half the aluminum are removed from the Keggin ion or replaced by some other element, such as boron or silicon. This will be investigated further with boron NMR. The direct ^{29}Si spectrum (Figure 2c) has 3 poorly resolved peaks, due to low concentration and thus poor signal:noise. The peak at -112 ppm, approximately 30% of the spectrum is an SiO_4 environment, is not directly linked to aluminum (no Al-O-Si bridges). The peak at -80 ppm is either a $\text{Si}(\text{OAl})_4$, $\text{Si}(\text{OAl})_3(\text{OSi})$ or a $(\text{SiO}_2(\text{OH})_2)$ specie, or a mixture. We will seek larger sample sizes for better signal:noise to resolve this uncertainty. These two environments of silica show that the both monomeric and polymeric silica is precipitated by alumina flocculation. The peak at -56.6 ppm is currently unidentified; perhaps associated with carbonate and/or calcium; since they are abundant in both cooling tower water and tap water. Identification of this peak warrants further study. Cross polarization (CP) ^{29}Si NMR experiments provide better signal:noise by enhancing relaxing via cross-polarization of protons. Thus the only signals that are enhanced are those of Si in close proximity to protons. The CP ^{29}Si NMR spectrum (Figure 2b) reveals that only the Si environment of $\text{Si}(\text{OAl})_4$, $\text{Si}(\text{OAl})_3(\text{OSi})$ or $(\text{SiO}_2(\text{OH})_2)$ is in close proximity to protons. This lends further evidence to the peak at -112 representing colloidal silica.

In summary, the aluminum Keggin cation remains mostly intact upon binding silica anions. Furthermore, only about $1/3^{\text{rd}}$ of the alumina cations present actually bind silica, which suggests the prehydrolyzed form of alumina is not necessarily the most effective for precipitating silica under these water conditions and form of dissolved silica. The ratio of monomeric (70%) to colloidal (30%) silica seen here probably reflects the state of the silica in these water conditions before the alumina is added.

Table 5
 ^{27}Al and ^{29}Si NMR chemical shifts for aluminosilicate floc

$\delta(^{27}\text{Al})$, ppm	Relative percent of integration
66.7	15.3
13.3	84.7
Direct $\delta(^{29}\text{Si})$, ppm	Relative percent of integration
-56.6	10.3
-80.6	60.5
-112.6	29.2
CP $\delta(^{29}\text{Si})$, ppm	Relative percent integration
-83.6	100

Figure 2a. ^{27}Al spectrum of the alumina flocculation of silica, using boroalumina coagulant

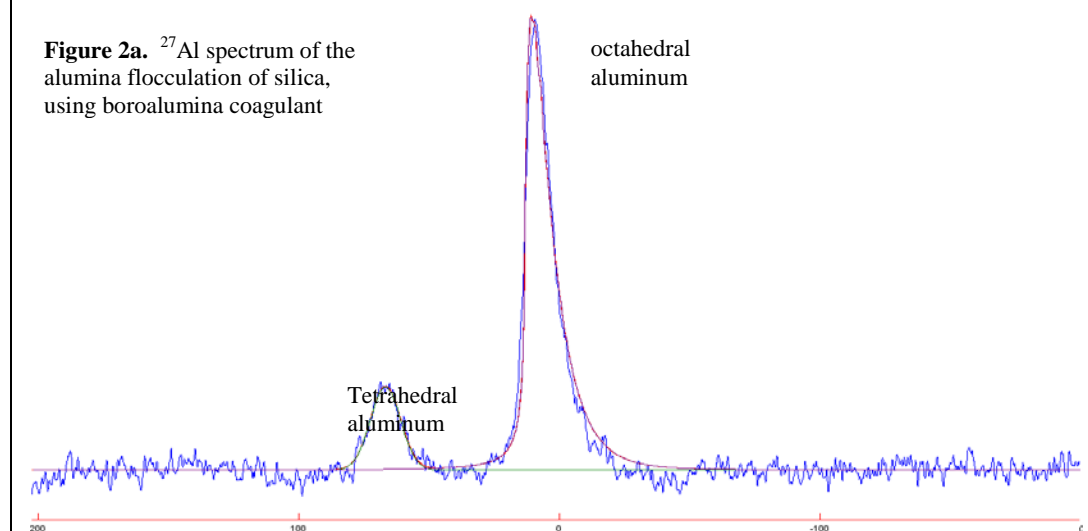


Figure 2b. Cross polarization ^{29}Si spectrum of the alumina floc containing silica.

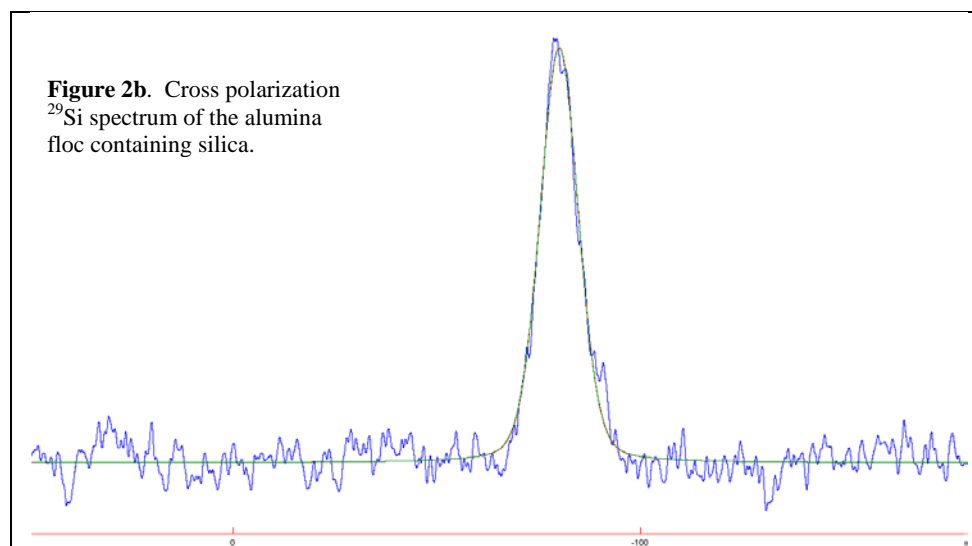
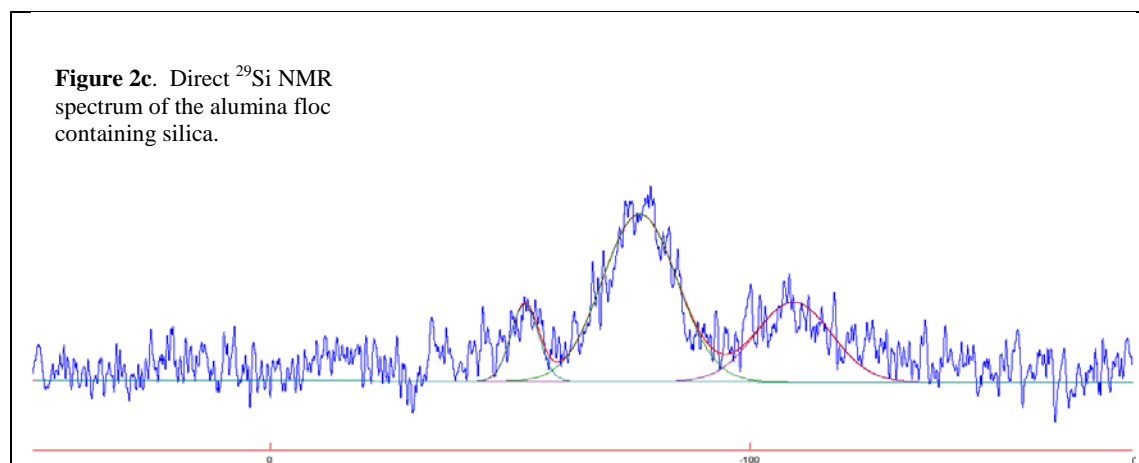


Figure 2c. Direct ^{29}Si NMR spectrum of the alumina floc containing silica.



Phase III. Considering Alternatives and Supportive Data

The success of PAX-18 was not considered a final solution to the challenge, as the extra cost of this specialty product (or any other PACL formulation) would be worth avoiding if more economical alternatives were found efficacious. PAX 18 is also not ideal in view of our first criterion (see section 1.2) concerning the amount of hazardous chemicals to be handled and inventoried, as its highly acidic nature requires that significant amounts of concentrated sodium hydroxide be used to correct the pH of water during treatment. Therefore, more commonplace aluminum compounds were explored.

The first alternative to be considered was aluminum chloride (AlCl_3), and the determination of favorable conditions for silica coagulation during Phase II was helpful in expediting our assessments. From this point forward, experiments all used minimally processed tap water, the same as that comprising make up water for cooling towers at SNL. Not only is make up water a more realistic target for silica removal by the proposed means, its use in experiments eliminates the possibly confounding effects of antiscalants that may be in tower water.

Results of the first test of AlCl_3 , shown in Table 6, immediately confirmed the possibility of more economical alternatives, and increased evidence that coagulation of silica was best performed near pH 8 rather than at some pH suggested by historical use of a particular coagulant. At that pH, an efficiency of 0.40 was obtained, coming close to the best achieved by PAX 18 at the same concentration.

Table 6
First Trial of Aluminum Chloride

Group	pH Before Treatment	pH During Treatment	mg. Al^{3+} as AlCl_3	Efficiency $\frac{\text{mg. SiO}_2}{\text{mg. Al}}$	Average Final Silica PPM
A	8.49	6.40	72	0.30	9.3
B	8.49	7.05	72	0.33	7.5
C	8.49	8.13	72	0.40	2.0

Note: AlCl_3 gives results comparable to PAX18 and superior to GaAl_2 at pH 8.13.

Testing AlCl_3 in different samples of untreated groundwater, efficiencies of 0.60 and greater were obtainable using lower doses of Al, and this was especially easy when the starting silica load was under 30 ppm.

Although flocs produced by AlCl_3 settled easily, they were noticeably smaller and lighter than those of other coagulants, such as GaAl_3 , even as silica removal by AlCl_3 was more efficient. It became obvious that the amount of silica in a floc was completely unrelated to its volume or density, as illustrated by the settled, coagulated water samples in Figure 3. In these examples, the dense ferric chloride-precipitated floc actually has the least amount of silica, and the tenuous BaI_2 floc contains more than the heavier one produced by GaAl_2 .

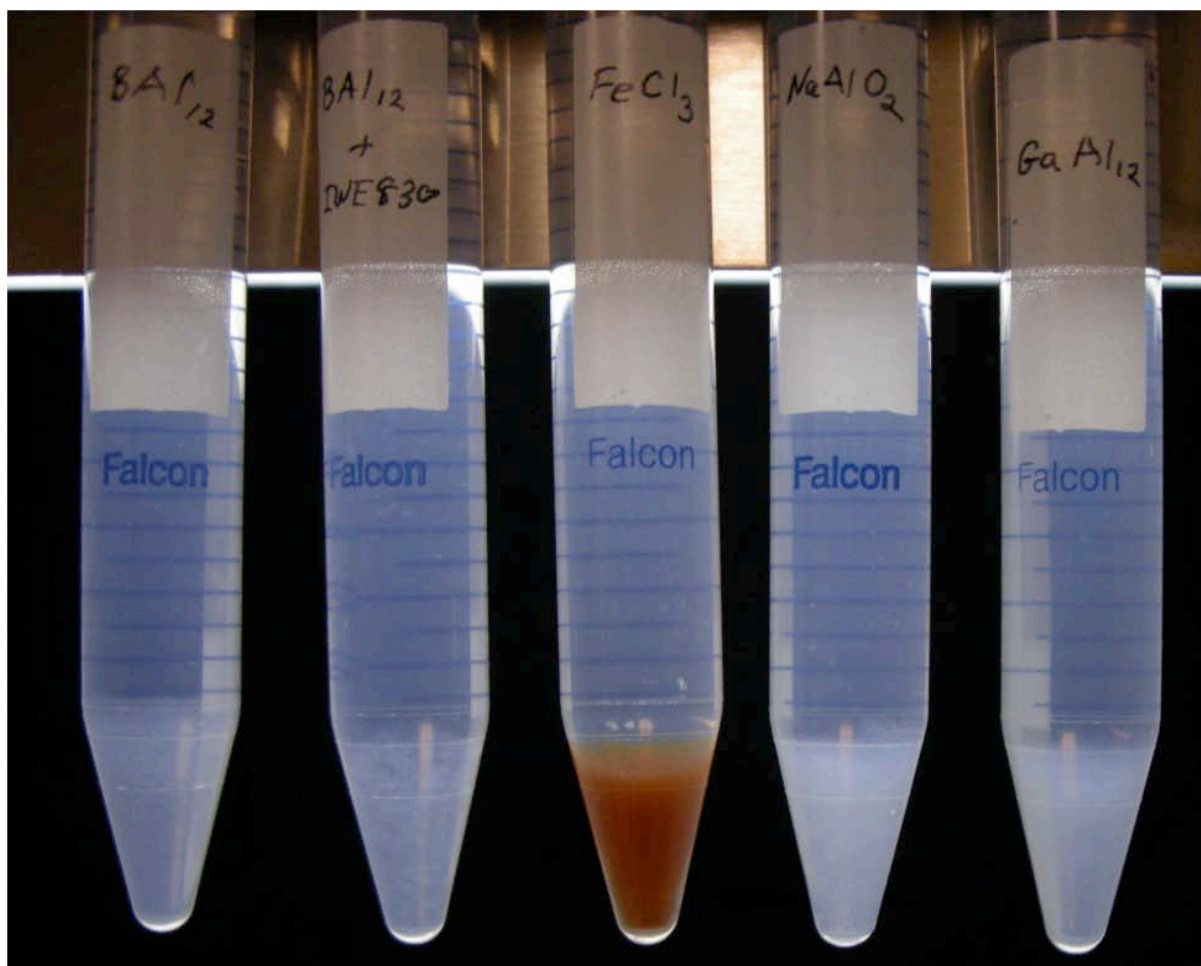


Figure 3. Settled floc examples in 12 mL water samples. Note that the heavy, brown material from FeCl_3 contains much less silica than the others of lighter appearance. Lighter flocs may be advantageous in producing less waste, provided they can be filtered out.

Analyses were performed to better understand the nature of differences in appearance of the materials flocculated by various coagulants and their effects on treated water in addition to removal of silica. As the GaAl_{12} floc appeared much larger than that of the more effective silica scavengers, PAX18 and AlCl_3 , a comparison was made first by drying and weighing the material precipitated from two 50-mL samples of tap water. The dry solids arising from the addition of 72 mg/L of Al as GaAl_{12} weighed 5.4 mg, while dry material precipitated by the same amount of Al as PAX18 weighed only 3.4 mg.

We analyzed the dried flocs by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and infrared spectroscopy (FTIR). The semi-quantitative elemental composition (from EDS) of the flocs is summarized in Table 7 below. There are a couple of interesting points to note in these results. First, the monomeric aluminum salt, AlCl_3 , precipitates much more silica on a per-mole aluminum-added basis. For the monomeric aluminum, Al:Si ratio in the floc is approximately 2:1 whereas it is closer to 6:1 for the GaAl_{12} , although the GaAl_{12} precipitates a greater total weight of material. Neither floc removes a significant amount of Ca, another

potential scale former, under the conditions of these experiments. Although there is relatively little sulfate in tap water, the GaAl_{12} floc seems to be selective for precipitating sulfate. Perhaps this is true of other anions as well, which may be a consideration for future research. The FTIR analysis also showed a stronger Si-O stretch for the monomeric aluminum salt floc than for the GaAl_{12} floc. This indicates a greater Si to Al ratio obtaining in the AlCl_3 floc, which corroborates the EDS and Hach data and confirms a more efficient coagulation with AlCl_3 .

Table 7
Relative proportions of selected elements in silico-alumina flocs
by SEM-EDS

Element	Relative Wt%
AlCl_3 Floc (3.4 mg)	
Al	68
Si	30
Ca	1.6
Total	100.00
GaAl_{12} Floc (5.4 mg)	
Al	74
Si	13
Ca	0.66
Ga	8.5
S	3.2
Total	100.00

Note the greater silicon to aluminum ratio obtained in the AlCl_3 floc, verifying the better efficiency of this coagulant.

The treated water separated from the flocs analyzed above was found to be reduced in alkalinity from the original 84 ppm to 74 ppm in both cases, suggesting some loss of calcium carbonate. Dissolved aluminum concentration was 0.36 ppm from AlCl_3 and 0.17 ppm from GaAl_{12} .

Since magnesium precipitation has been implicated in silica removal under alkaline conditions, and the intentional addition of magnesium as a potential aid to flocculation had been attempted in Phase II with equivocal results, an experiment was done using the promising aluminum chloride coagulant with and without added magnesium, and pH adjustment. Refer to Table 8 for the experimental setup and results.

The native magnesium content of the tap water to be treated was 6 ppm by ICP-mass spectrometry, and for selected 100-mL containers of water was supplemented with 2 mM MgCl_2 to 54 ppm. Every container except the untreated control (container F) received an amount of NaOH predetermined to result in a pH of 8.1 during coagulation, and all treated containers except container A received it before the addition of AlCl_3 . Therefore, all containers except A and untreated control F were exposed to a pH of 10.6 or higher before coagulation. A pH of 10.5 or higher precipitates magnesium. One container (E) was treated only with NaOH and no aluminum coagulant to see if Mg precipitation in itself adequately removes silica.

Test containers were also split between those receiving dry AlCl_3 and those receiving it as a liquid concentrate to see if the form of the coagulant makes a difference.

Table 8
Magnesium, pH, and Aluminum-Silica Coagulation

Container	pH Before Treatment	pH During Treatment	Starting Mg^{2+} PPM	AlCl_3 Dry or Liquid	$\frac{\text{Wt. SiO}_2}{\text{Wt. Al}}$ (72 ppm)	Final Silica PPM
A	7.97	8.1	54	Dry	0.41	2.5
B	10.60	8.1	54	Dry	0.43	1.5
C	10.60	8.1	54	Liquid	0.43	1.4
D	11.47	8.1	6	Liquid	0.44	0.6
E (NaOH only)	11.42	8.1	6	None	N/A	25.1
F (Not Treated)	7.99	7.99	6	None	N/A	32.1

Note that coagulation in containers with extra magnesium have no better result than those without (eg., C vs. D), and that magnesium precipitation by NaOH alone (E) provides insufficient removal of SiO_2 . NaOH pretreatment increases SiO_2 removal by about 1 ppm (A vs. B).

All silica reductions in this experiment were over 90%. Magnesium may have helped achieve that, but a period of high alkalinity was more important than was excess magnesium supplementation. There was no difference between AlCl_3 added as a liquid or as a dry chemical. And the effect of magnesium precipitation alone (no Al) was noted in container E as a 22% (7 ppm) reduction in silica.

This experiment, and others providing similar results, showed that the extra procedure of raising the pH of raw water to a very alkaline condition, before the acidic aluminate coagulant reduces it again may provide an additional silica reduction of up to 2 ppm due to magnesium precipitation, or a total of 7 ppm without any other coagulant added. One drawback to this, in addition to the trouble of adjusting pH twice and the use of concentrated NaOH, is that unlike the heavy flocs produced by aluminum coagulation, the $\text{Mg}(\text{OH})_2$ precipitate is very fine and does not consolidate and settle quickly. Figure 4 demonstrates how this might present a problem to speedy separation of the contaminants by either settling or filtration through a coarse medium like sand.

Since it has been claimed that the practice of soda-lime water softening by certain municipalities results in sufficient silica reduction, this was not overlooked in order to better evaluate the results of our experiments with aluminum-based coagulants. Although we could not reproduce the closed, superheated system available to some utilities, we did subject groundwater, with a dissolved silica content of 34.5 ppm for up to 6 hours to 90°C, calcium hydroxide at 150 mg/L and sodium carbonate at 70 mg/L, with and without 35 ppm aluminum as AlCl_3 . The results are displayed in Table 9, and show that the coagulant alone achieved a reduction of 79% of silica, with an efficiency quotient of 0.78. In water with supplemental magnesium and soda-lime

treatment, the silica reduction improved from 15% to 37% in 6 hours of heating, while soda-lime without supplemental magnesium appeared totally ineffective at 30 minutes and was not resampled.

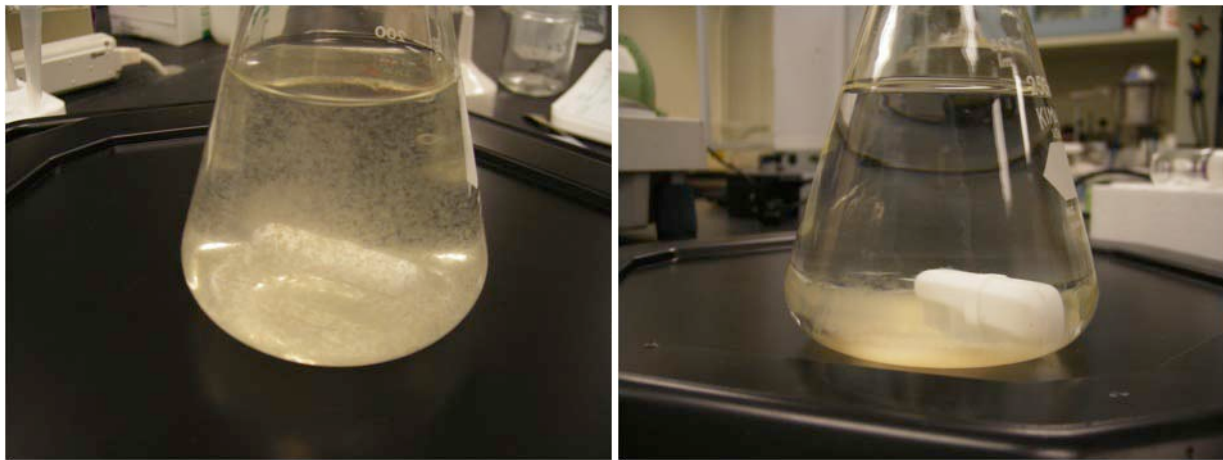


Figure 4a. Flocculation by polyaluminum coagulant in flasks, immediately after (left) and 20 minutes after (right) the end of stirring, **showing rapid settling of the floc and water clarity.**



Figure 4b. Precipitation of magnesium hydroxide and silica by NaOH immediately after (left) the end of stirring, and only gradual clearing in progress 20 minutes later (right). **The lingering haze of fine particulates may be more difficult to remove by sand bed filtration than is the alumino-silicate floc seen above in Fig. 4a.**

Table 9. Soda-Lime Water Softening for Silica Reduction vs. AlCl_3

Container	Treatment	Heating Time (90°C)	Final Silica PPM	Percent SiO_2 Removed
A	35ppm Al as AlCl_3 , 54ppm Mg, no soda-lime*	None	7.3	79%
B	soda-lime softening, 54ppm Mg, 35ppm Al as AlCl_3	30 minutes	9.0	74%
C	soda-lime softening, 54ppm Mg	30 minutes	29.1	15%
C resampled	soda-lime softening, 54ppm Mg	6 hours	21.7	37%
D	soda-lime softening, no added Mg (6 ppm only)	30 minutes	34.2	0

* Before adding AlCl_3 , pH was adjusted to 10.7 with NaOH to match the pH experienced by soda-lime treated water.

Phase IV. Sodium Aluminate and Process Optimization

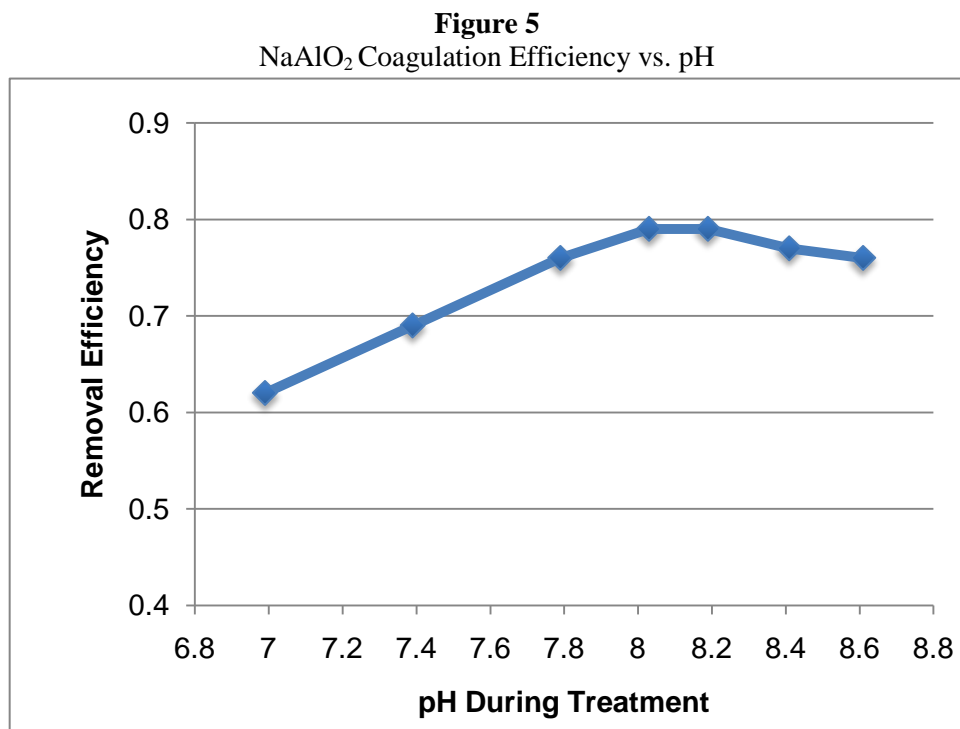
A corporate-sponsored study by Lindsay and Ryznar in 1939^[10] reported that sodium aluminate (NaAlO_2), one of the less expensive monomeric aluminum compounds, could be useful in removing silica from water if pH was controlled properly, but sodium aluminate has not received much attention in the literature in recent times. It is of special interest because it is the only readily available, readily soluble, aluminum-based coagulant that is not acidic and would not require a caustic reagent like NaOH in order to be used routinely. We found that at useful concentrations, it elevated the pH of tap water to a little over nine, which was correctable to a pH more amenable to SiO_2 coagulation with a very small amount of hydrochloric or sulfuric acid. Floc formation was rapid and silica removal was on par with other aluminum coagulants. Table 10 shows results of water treatment with a range of NaAlO_2 concentrations and no Mg added.

Table 10
Concentration ranging experiment for SiO_2 coagulation with NaAlO_2

Al ppm as NaAlO_2	Initial pH	Final adjusted pH	SiO_2 ppm Removed	Percent of SiO_2 Removed	Removal Efficiency mg SiO_2 /mg Al
17.5	8.85	8.18	19.7	56%	1.13
35	9.13	8.13	28.7	82%	0.82
52.5	9.33	8.17	32	91.4%	0.61
70	9.50	8.15	33	94.3%	0.47

It is obvious that the efficiency of silica removal increases with lower sodium aluminate doses, though the absolute capacity for coagulation becomes limited. If a user can accept silica removal at the 80% level, a 1:1 loading of aluminum to silica is feasible, with the prospect of low residual aluminum in the water and economy in the use of the coagulant, of acid, and with no need for NaOH. The resulting water would be ready for industrial use, or even drinking, without any readjustment of pH.

As the ideal pH for coagulation may differ from one coagulant to another, it was decided to test sodium aluminate over a wider pH range in the interest of optimization and determining tolerance in the system. Table 11 gives the results.



From this experiment, the ideal pH range appears to be from pH 8.0 to 8.2, which is not surprising in view of the earlier investigations. In addition, the system appears to be broadly tolerant from pH 7.8 to 8.6 with only small efficiency losses at either end.

4 RESULTS SUMMARY

In exploring the efficacy of numerous coagulants and methods reputed to remove silica from water, we first expressed relative successes as the weight percent of silica removed from solution. However, as we progressed to trials in waters with a range of dissolved silica concentrations, it became more meaningful to turn to an efficiency quotient (ppm of SiO₂ removed over ppm of aluminum used). In the end, additional factors must be considered, including expense and ease of use. Table 11 presents the relevant information on the notable candidates tested in the study.

Table 11. Comparison of Coagulants and Processes

Coagulant or Process	Best % SiO ₂ removal	Efficiency as ppm SiO ₂ /ppm Al	Optimizing Conditions	Other Considerations
Al ₁₃	56	0.24	pH 8.0 – 8.2	Not yet commercially available
GaAl ₁₂	52	0.22	pH 8.0 – 8.2	Not yet commercially available
GeAl ₁₂	69	0.30	pH 8.0 – 8.2	Not yet commercially available
Boroalumina	70	0.36	pH 8.0 – 8.2	Not yet commercially available
Na Molybdate*	95	0.05	pH <4	expensive
PAX10*	45	0.67	Added surfactant pH 8.7	proprietary
PAX18	99	0.43	pH 8.0 – 8.2	Proprietary, greatly acidifying, large NaOH demand
AlCl ₃ **	92 - 98	0.41 - 0.44	pH 8.0 – 8.2	Acidifying, NaOH demand
NaAlO ₂	94	0.47	pH 8.0 – 8.2	Slightly alkalizing, small H ₂ SO ₄ demand
Magnesium precipitation	22	0.15 (SiO ₂ / Mg)	pH > 10.5	Slow to ppt and settle, NaOH demand
Soda-lime softening	37	N/A	Temp. ≥100°C	Large energy and facility demand

*Molybdate and PAX10 were only tested on concentrated tower water, while data from other candidates comes from tap water. Larger amounts of SiO₂ are available for capture from tower water.

**The efficiency range for AlCl₃ reflects difference between alkali pretreatment (pH >11) or not, with the pretreatment giving a slightly better outcome.

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5 CONCLUSIONS

1. Coagulation with aluminum-based chemicals can provide an uncomplicated way to remove silica specifically from industrial water, without investment in a complete water treatment process.
2. This technology does not require heating, pressure containment, or large energy expenditures, but only brief mixing and then settling or filtration, such as through standard depth filtration with sand and anthracite. Coagulation may be put “in-line” to minimize the footprint of the added step at an established facility^[11].
3. The water resulting from this process remains at a pH similar to original ground or surface water, and does not contain large amounts of residual chemicals. Therefore it is compatible with other uses and safe discharge.
4. An operating pH of 8.0 to 8.2 is optimal for coagulation with these products, yet the system is tolerant of minor pH changes from 7.8 to 8.4.
5. If 80% removal of silica present in typical make up water is acceptable, it can be done economically in terms of materials needed and may provide up to a five times extension of the period between blowdowns. Greater amounts of silica may be removed at an additional cost in efficiency.
6. Sodium aluminate is favored as a coagulant because it is available as a concentrated liquid, is not proprietary, and requires the least demand for pH adjustment of the chemicals tested.
7. The criteria listed in Section 1.2 appear to be achievable by further development of the methods explored in this study.

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6 LOOKING FORWARD

The promising results of this investigation in coagulation as a means of removing silica from water to theoretically preempt the formation of silica scale on downstream equipment lend themselves to further development in order to better understand how this technology could be implemented at an industrial scale and to anticipate its costs and other implications. The next steps from a research standpoint might include the following:

- Focusing on the use of sodium aluminate, develop methods for further reducing the amount of residual aluminum in the finished water.
- It has been stated that residual aluminum may facilitate the deposition of any remaining silica as silico-aluminate scale. Address this potential problem with a systematic experimental program, utilizing a lab-scale nanofiltration system, which is sensitive to silica fouling, as a model.
- Determine the other factors affecting the efficiency of silica coagulation, with the possibilities of temperature, hardness, and common metallic contaminants of water as factors.
- Some reduction of alkalinity was seen in results of silica coagulation. Can this be increased and exploited to eliminate significant amounts of carbonate, another scale-forming solute?
- If sodium aluminate remains attractive, determine real-world costs of a continuous supply in the amounts needed, and the volume of sludge potentially resulting from the process of coagulating make up water for cooling towers.
- If the use of sodium aluminate remains feasible after the economic analysis, design and run a pilot test.

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7 REFERENCES

- [1] Behrman, A.S. and A. Gustafson, Removal of Silica from Water, *Industrial and Engineering Chemistry*, 32 (1940) 468-472.
- [2] Sheikholeslami, R., I.S. Al-Mutaz, T. Koo, and A. Young, Pretreatment and the effect of anions and cations on prevention of silica fouling, *Desalination* 139 (2001), 83-95.
- [3] Al-Rehaili, A.M., Comparative chemical clarification for silica removal from RO groundwater feed, *Desalination* 159 (2003), 21-31.
- [4] Nyman, M., D. Ingersoll, S. Singh, F. Bonhomme, T.M. Alam, C.J. Brinker, and M.R. Rodriguez, Comparative study of inorganic cluster-surfactant arrays, *Chem. Mater.* 17 (2005), 2885-2898.
- [5] Qin, J., M.H. Oo, K.A. Kekre, F. Knops, and P. Miller, Impact of coagulation pH on enhanced removal of natural organic matter in treatment of reservoir water, *Separation and Purification Technology* 49 (2006), 295-298.
- [6] Kvech, S. and M. Edwards, Solubility controls on aluminum in drinking water at relatively low and high pH, *Water Research* 36 (2002), 4356-4368.
- [7] Stewart, T.A., D.E. Trudell, T.M. Alam, C.A. Ohlin, S. Jett and M. Nyman, Enhanced water purification: a single atom makes a difference, *Environmental Science and Technol.* 21 (2009), 2201-2208.
- [8] de Freitas, A.S.W., A.W. McCulloch and A.G. McInnes, Recovery of silica from aqueous silicate solutions via trialkyl or trialkylammonium silicomolybdate, *Can. J. Chem.* 69 (1991) 611-614.
- [9] Brace, R., and E. Matijevic, coprecipitation of silica with aluminum hydroxide, *Colloid and Polymer Sci.* 255 (1977), 153-160.
- [10] Lindsay, F.K., and J.W. Ryznar, Removal of Silica from Water by Sodium Aluminate, *Industrial and Engineering Chemistry* 31 (1939), 859-861.
- [11] Huang, H., K. Schwab and J.G. Jacangelo, Pretreatment for low pressure membranes in water treatment: a review, *Env. Sci. and Technol.* 43 (2009), 3011-3019.

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