On-site production of a silica-based microparticulate retention and drainage aid

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ABSTRACT: Silica-based microgels are shown to be different from conventional colloidal silicas in physical structure and performance as retention and drainage aids in papermaking. Reductions in the required silica dose of 50% or more have been demonstrated in mill trials when using polysilicate microgel solution to replace colloidal silica. The polysilicate microgel solution is manufactured at the paper mill from commodity chemicals using a simple process. The critical conditions for microgel formation and performance are discussed.

KEYWORDS: Additives, drainage aids, gels, on site operations, retention aids, silica gel, wet end additives.

Background

Microparticulate retention and drainage aids are becoming increasingly popular. Among the commercial microparticulates, colloidal silica is one of the most popular and most effective. Over the past five or six years, however, a number of patents have been issued which claim silica-based "microgel" solutions are more effective retention and drainage aids than conventional colloidal silica on a specific weight basis. Silica-based microgels that have been disclosed in the patent literature have included polyaluminosilicate, polysilicic acid, and polysilicate microgels. All of these microgels are distinct from colloidal silica not only in performance but also in physical structure. As shown in **Fig. 1**, colloidal silicas are composed of discrete spheres of silica, whereas microgels are composed of smaller silica particles which are linked together to form a three-dimensional microgel network.[1] Silica microgels have been utilized for over 50 years in other industrial applications and are often referred to as "active" silica in the open literature.

The conventional colloidal silicas used as retention and drainage aids in papermaking are generally about 3–5 nm in diameter and have a specific surface area of about 500–600 m^2/g. The solutions are usually prepared by deionization of a sodium silicate solution to produce silicic acid. The silicic acid is condensed to form particles 1–2 nm in diameter and then grown under specific conditions to produce the desired diameter colloids. The colloidal silica solution is chemically stabilized to prevent further growth or gellation. Iler graphically depicts this process in his book, *The Chemistry of Silica*,[1] as shown in **Fig. 2**. The 1–2-nm particles produced by the polymerization of the silicic acid are frequently referred to as polysilicic acid in the open literature. This product is not the same as a polysilicic acid microgel because the polysilicic acid particles are again individual discrete spheres of silica, not a three-dimensional gel network.

Many different methods for preparing microgels are disclosed in U.S. patent 4,954.220.[2] This patent covers the use in papermaking of silica microgels when used in conjunction with a cationic polymer. The two preferred methods for preparing microgel solutions are deionization of sodium silicate solution or direct addition of an acid to neutral-

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[1]Iler, R., *The Chemistry of Silica*, John Wiley and Sons, New York, 1979.

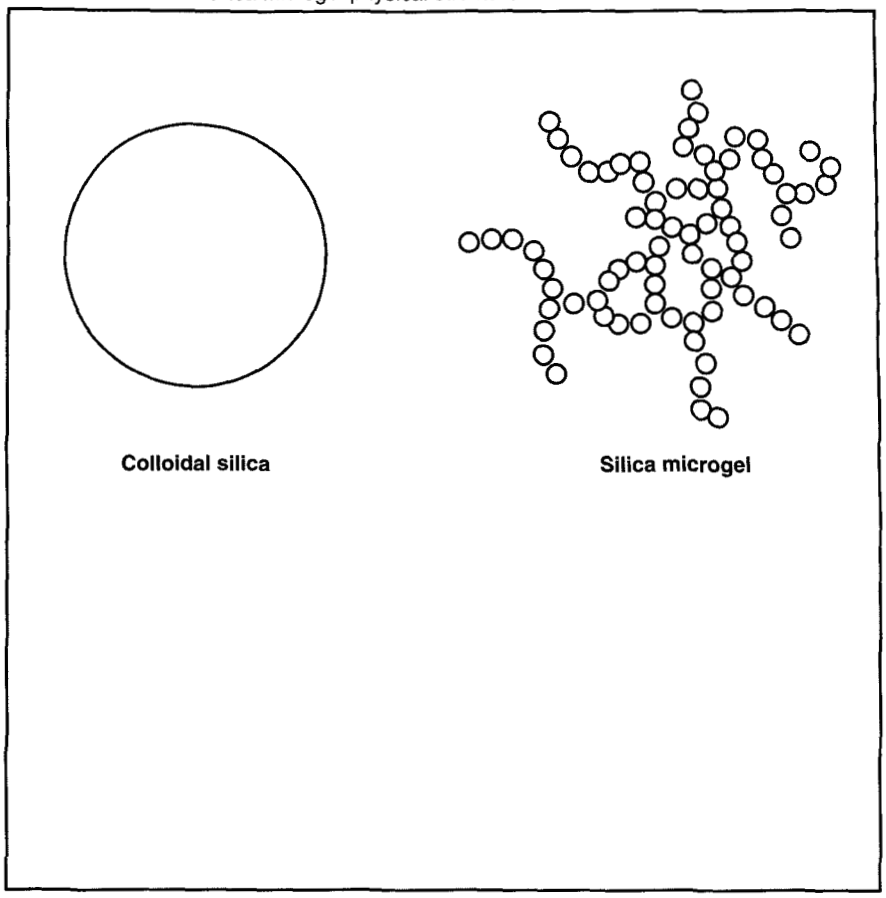
[2]Rushmere, J. D., U.S. pat. 4,954,220 (Sept. 4, 1990).

ize all or part of the sodium oxide present in the silicate solution. Both methods initiate polymerization of the silica which results in the formation of silica particles 1–2 nm in diameter. With time, these particles begin to link together to form three-dimensional microgel networks, as shown in Fig. 2. Typically microgels produced by these methods have specific surface areas of about 1200 m^2/g, or about 2–2.5 times the specific surface area of colloidal silica used in papermaking.

The surface of both colloidal silica and silica microgels are covered with hydroxyl groups. These hydroxyl groups can ionize in a water solution above pH 2 such that the silica particles become anionic, as shown in **Fig. 3.** The extent of ionization of the hydroxyl groups is pH dependent. It is this anionic surface charge which permits the colloidal silica or microgels to flocculate a paper furnish which has been made cationic by the addition of other chemicals. Because microgels have 2–2.5 times the spcific surface area of conventional colloidal silica, they also have about 2–2.5 times the anionic charge equivalence per unit weight. This is why only 40% or 50% as much silica in microgel form is needed to provide the same level of retention and drainage as when silica is in the form of a conventional colloid.

Both colloidal silica and microgels have a maximum silica concentration above which the silica particles will either grow in size or gel as shown in **Fig. 4.**[1] The 3–5-nm colloidal silica sols used in papermaking are stable with up to as much as 15 weight percent SiO_2. Stable sloutions with higher SiO_2 concentrations are commercially available, but these solutions contain larger diameter silica particles. By increasing the diameter of the silica particles, the specific surface area and hence the specific anionic charge are reduced. This results in the need to use higher amounts of silica to maintain a given level of retention and drainage.

1. Colloidal silica vs. silica microgel physical structure

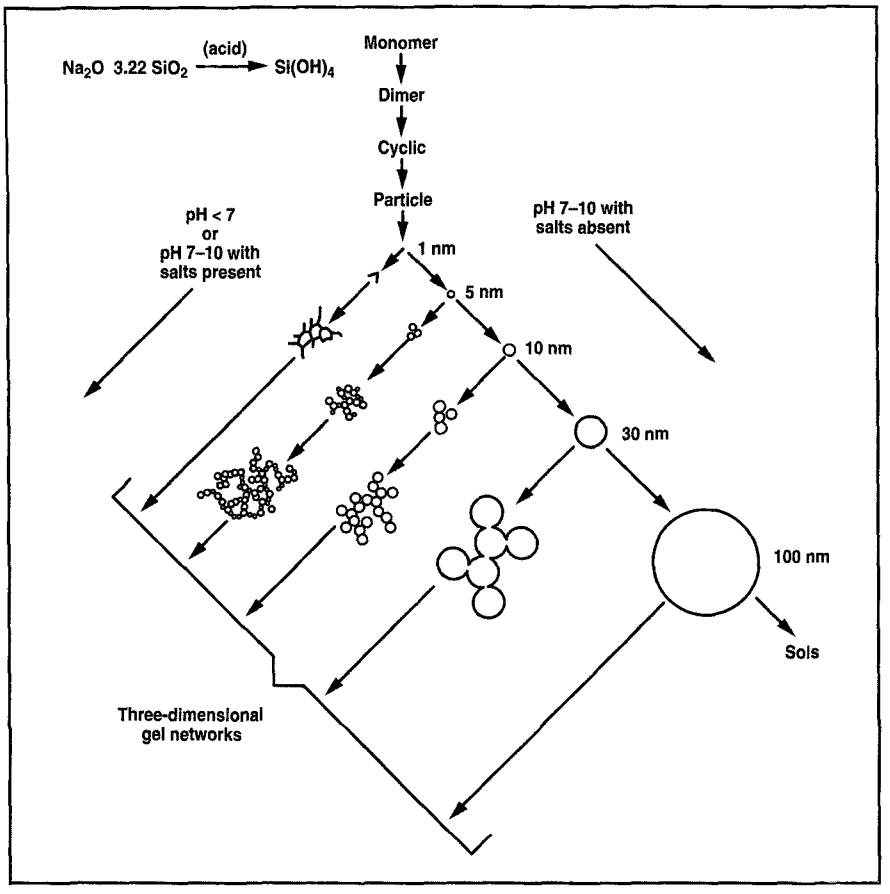


Comparatively, 1-nm colloidal silica solutions are only stable when containing one weight percent SiO_2 or less. One nanometer silica particles have much greater specific area and anionic charge than the 3–5-nm colloids used in papermaking, but tests have shown that these 1-nm diameter particles are not very effective as a retention and drainage aid. However, by linking these 1-nm diameter particles together to form a microgel, the solution becomes an extremely effective retention and drainage aid! The maximum stable silica concentration, however, is still about one weight percent. Therefore it is economically impractical to manufacture silica microgel solution at a central plant site and ship it to paper mills for use. To utilize the economic and performance benefits of the silica-based microgel technology, a simple process was needed to *convert sodium silicate solution into* a microgel solution at the paper mill. This would give the mills the freedom to purchase commodity chemicals and generate from them a high-performance retention and drainage aid.

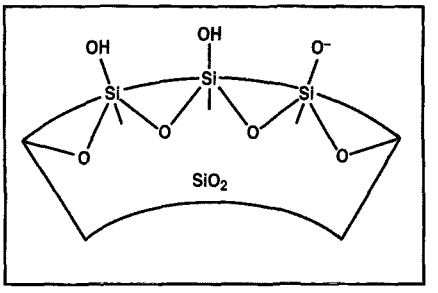
Process development

Most of the microgel solutions used during the initial chemical technology development were prepared by the deionization of sodium silicate solution. Microgels formed by this process have been shown to perform extremely well and are quite stable with time. The deionization process normally entails feeding silicate solution containing less than or equal to 5% SiO_2 through an ion exchange resin bed such that silicic acid exits the column at approximately pH 3. The silicic acid solution is then aged to permit microgel formation, and

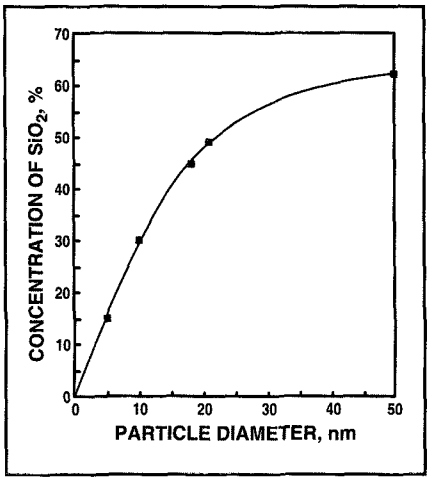
2. Polymerization of silica



3. Silica particle surface



4. Maximum stable SiO_2 concentration vs. particle size



finally the solution is diluted to ≤ 1% SiO_2 to stabilize it. The product thus formed is a polysilicic acid microgel solution. This process is similar to the manufacturing process used for colloidal silica. Experience has shown this process requires the attention of a full time operator and therefore would be impractical for an unsupervised process at a paper mill.

Of the other methods disclosed in U.S. patent 4,954,220 to prepare microgel solutions, the use of sulfuric acid is considered the most practical for use in a commercial process. Sulfuric acid is widely available, inexpensive, and the sodium sulfate produced from the reaction of sulfuric acid with sodium oxide is compatible with the papermaking process. A very important additional benefit is that the sodium sulfate acts as a catalyst for microgel formation.

When using sulfuric acid to produce silica microgels, the process becomes amenable to full automation, it essentially becomes an acid/base titration. However, appropriate process conditions for the reaction must still be selected. There are three process variables that can be manipulated which can dramatically affect the microgel formation and performance. They are:

- The extent of sodium oxide neutralization in the sodium silicate solution—a pH dependent reaction
- SiO_2 concentration of the sodium silicate solution
- The length of time the solution is allowed to age after acid addition and before final dilution to stabilize the microgel.

Optimal operating conditions are selected to produce microgel solutions that quickly achieve a high level of performance without permitting polymerization to generate a silica gel throughout the solution.

To test microgel performance, one of the simplest and best methods is the use of the Canadian Standard Freeness (CSF) test. The CSFdata for this paper were developed using an alkaline bleached kraft furnish composed of 56% hardwood, 14% softwood, and 30% precipitated calcium carbonate. Consistency was 3 g/L and pH was 8.0. All tests were conducted by adding 20 lb/ton of cationic potato starch (0.03 DS) to the furnish in a Britt Jar followed by the addition of the microgel solution. The flocculated furnish was then tested for freeness.

All of the microgels in this study were prepared from 41° Baume sodium silicate solution with a SiO_2:Na_2O ratio of 3.22:1.0. All concentrations reported are weight percents.

Microgels

The first test series was conducted to demonstrate how neutralizing a silicate solution to a different extent can dramatically affect the rate of microgel formation and its performance. The microgel solutions were prepared from sodium silicate solutions containing 2.0% SiO_2. Five normal (5*N*) sulfuric acid was added to reduce the silicate pH to different levels. The solutions were allowed to age for 5 min after the acid was added and then diluted to a concentration of 0.125% SiO_2 to prevent further microgel formation. As can be seen from the sodium silicate/sulfuric acid titration curve in **Fig. 5**, the neutralization process between pH 8 and 3.5 is very rapid. Therefore, pH 3, 9, and 10.5 were selected as practical operation conditions. The pH-3 microgel is correctly classified as a polysilicic acid microgel, whereas the pH-9 microgel is termed a polysilicate microgel. The open literature suggests the pH-10.5 solution is still essentially a silicate solution with little or no microgel formation having occurred. **Figure 6** shows the pH-9 polysilicate microgel solution produces the greatest freeness in the test furnish. The pH-3 polysilicic acid microgel solution shows very little performance when formed under the conditions used in this test series. However, the third test series described in this paper shows that polysilicic acid microgels can yield good performance when formed under different conditions.

The second test series examined the effect of SiO_2 concentration during the acidification step and aging period. Silicate solutions containing 0.5%, 1.0%, 2.0%, and 3.0% SiO_2 were acidified to pH 3 and 9, aged 5 min and then diluted to 0.125% SiO_2. A 4.0% SiO_2 solution was not tested because it gels in as little as one minute at pH 9 and is therefore an impractical operating condition. **Figure 7** shows that increasing SiO_2 concentrations, up to 2% SiO_2, yields microgels producing higher freeness in the test furnish. At 3% SiO_2, the sample is beginning to gel throughout the solution by 5 min and, as a result, its performance is decreased. Note again that the polysilicic acid microgel solution prepared at pH 3 does not give the same level of performance as the polysilicate microgel solution prepared at pH 9.

The third test series demonstrates the development of maximum performance with time with microgels formed at pH 3 and 9. Both microgels were prepared from a 2.0% SiO_2 solution and acidified with 5*N* sulfuric acid. The solutions were allowed to age to the specified time and then diluted to 0.125% SiO_2. **Figure 8** shows the polysilicic acid microgel solution prepared at pH 3 takes 24 h or more to reach its maximum per-

I. Mill trials using polysilicate microgel solution

Trial A
Paper type: alkaline fine paper
Former: twin wire, 700 ton/day
Paper grades: coating base
Basis weights: 55 - 183 lb/3300 ft² (7 different weights manufactured)
Wire speed: 3140-2450 ft/min
Sheet ash: 16-19%

Reference System:
- 0.5 - 2.0 lb/ton colloidal silica
- 10 - 30 lb/ton cationic waxy maize-starch
- 2.0 - 0.5 lb/ton anionic polyacrylamide solution.

Polysilicate Microgel System:
- 0.25 - 1.0 lb/ton polysilicate microgel
- Equal cationic waxy maize starch dose
- Equal anionic polyacrylamide solution dose.

Results:
- 50% reduction in amount of SiO_2 required
- First pass retention equal
- Ash retention equal

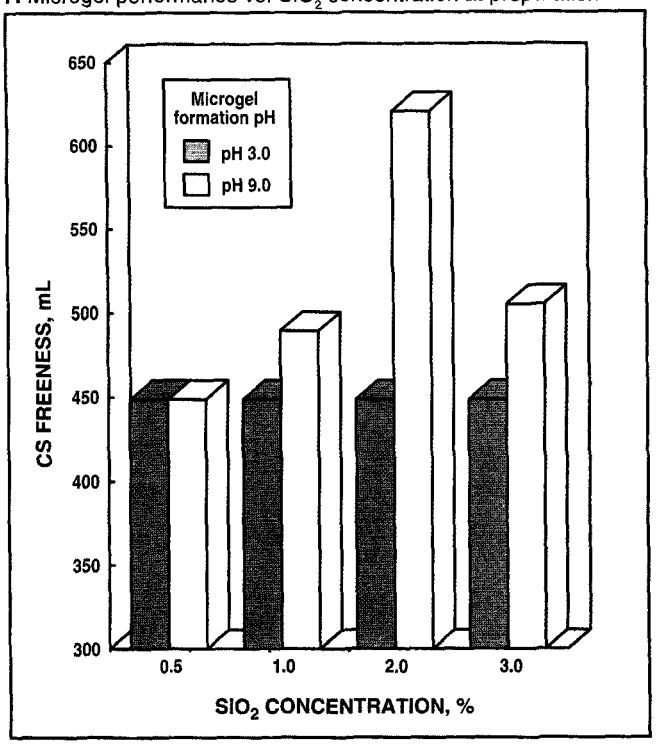
Trial B
Paper type: alkaline fine paper
Former: fourdrinier, 400 tons/day
Paper grades: coating base, copy
Basis weights: 46 - 73 lb/3300 ft² (3 different weights manufactured)
Wire speed: 2100-1300 ft/min
Sheet ash: 14%

Reference System:
- 0.58 - 2.2 lb/ ton colloidal silica
- 11 - 33 lb/ton cationic potato starch

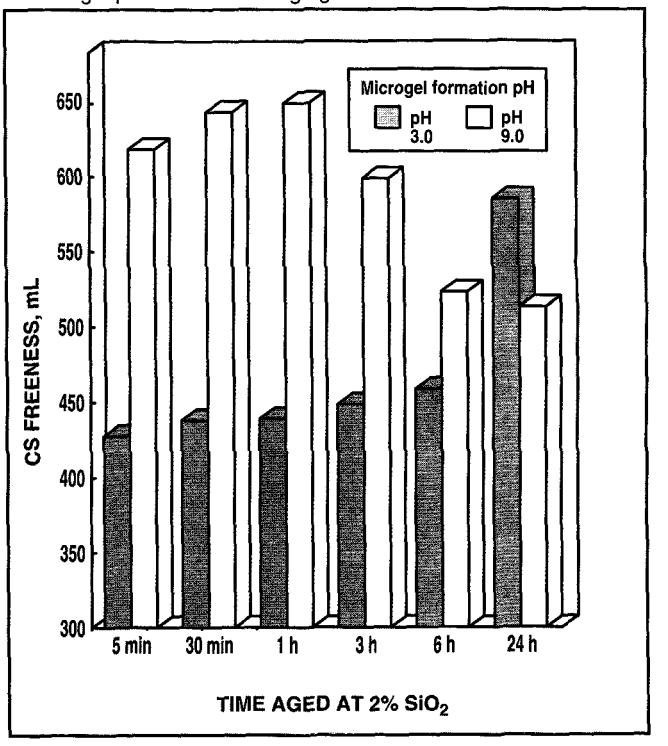
Polysilicate Microgel System:
- 0.23 - 0.88 lb/ton/polysilicate microgel
- Equal cationic potato starch dose

Results:
- 60% reduction in amount of SiO_2 required
- First pass retention equal or improved
- Ash retention equal or improved.

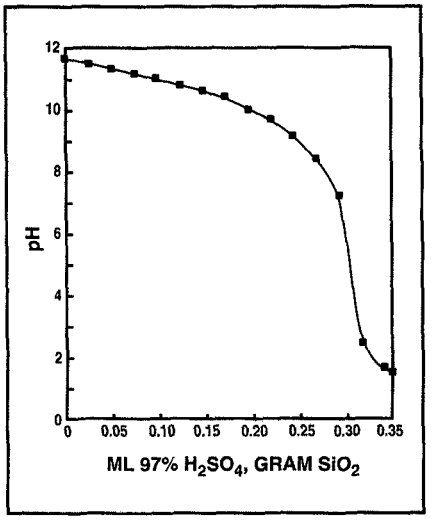
7. Microgel performance vs. SiO_2 concentration at preparation



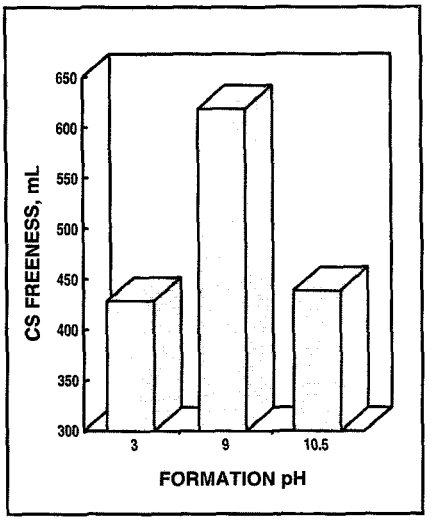
8. Microgel performance vs. aging time



5. Titration of sodium silicate solution (2% SiO_2) with sulfuric acid



6. Microgel performance vs. formation pH



formance, whereas the pH 9 polysilicate microgel solution reaches 95% of its maximum performance 5 min after the acid is added. Note, however, that the polysilicate microgel solution begins to lose significant performance by 6 h. Again, this is the result of continued gellation and loss of surface area. This loss of performance can be arrested by diluting the microgel to < 1% SiO_2.

Using the above data a proprietary microgel generator was constructed to demonstrate the manufacture of polysilicate microgel solution at a paper mill. The machine is commonly referred to as the Mark 2 generator and utilizes commodity grade sulfuric acid and sodium silicate. The generator may be run as either a continuous or a batch process. It is capable of feeding up to a 1000-tons/day paper machine or multiple smaller machines. The generator is fully automated and requires little or no attention from an operator. It is a stand-alone system, but may optionally be integrated into a DCS system if desired. The generator incorporates redundant processing lines for assured reliability and an automatic flush cycle to remove any silica deposits which might form in the processing lines. The Mark 2 generator continually conducts two automatic quality control measurements to ensure the performance of microgel solution.The process has been successfully used in extended trials at multiple customer sites during which the generators demonstrated routine manufacture of quality polysilicate microgel solution with minimal attention.

Mill trials

Table I presents the results from two extended trials in which polysilicate microgel solution was manufactured at the paper mill site using the above process. The objective of both trials was to substitute polysilicate microgel solution for the colloidal silica used on the paper machines while maintaining all other operating conditions on the paper machine. No paper machine optimization program was conducted in either trial. Both trials demonstrated 50% or greater reduction in the amount of SiO_2 required when using polysilicate microgel solution instead of colloidal silica.

Conclusions

Silica-based microgels are different from colloidal silica:

- Microgels are three-dimensional chained networks of 1–2-nm diameter silica particles, whereas colloidal silica is individual larger silica particles.
- Microgels have 2–2.5 times the specific surface area and hence 2–2.5 times the specific anionic charge of conventional colloidal silica used in papermaking.
- Selection of the proper operating conditions is critical for microgel formation and performance.
- Manufacture and use of polysilicate microgel solutions at paper mills by a fully automated unit is a practical alternative to the use of other retention and drainage aids.
- Polysilicate microgel solutions manufactured at paper mills have at least two times the efficacy of colloidal silica.

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