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Novel Cohesive Cement Sealant System

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Abstract

This paper documents development of a unique sealant that has strong cohesive properties. The cohesive nature of this system allows it to stay together as a complete fluid without being diluted by the fluids surrounding it. This is accomplished through a combination of stimulation and cementing chemicals and techniques. The properties of this cohesive sealant are applicable for lightweight system stability, plug and abandonment cement plug cohesiveness, balanced plug stability, and situations where the sealant must migrate through another fluid before it sets.

This fluid is particularly useful in applications requiring a lightweight sealant to float above another fluid. Traditional lightweight cement systems will disperse, allowing their particulates to separate from the system. The cohesive system developed is capable of holding its particulates in the system. In addition, this system develops higher compressive strengths than traditional lightweight systems.

The cohesive cement system was originally designed to be injected into a brine filled cavern, rise through the brine, and seal the top of the cavern. This was the reasoning for the cohesive nature of the system, its low density, and its high strength. The cohesive system was successful for this field application. The novelty of this system spurred further developments including expanded density ranges and mechanical property improvements, thereby broadening the range of utility for this system.

Introduction

Difficult circumstances often drive development of novel methods and materials to alleviate the difficulty. This is one such case. The difficult circumstance was created by a flow channel encountered in a well during drilling that could not be directly accessed. The situation required an oilfield sealant that could be placed into a well as a liquid, float up through several hundred feet of saturated sodium chloride (NaCl) brine, and seal the flow channel.

This application required a sealant unlike any currently used in the industry, and a focused research effort resulted in a hybrid material composition that met the design criteria. This hybrid composite combined oil well cement chemistry with fracturing fluid chemistry to produce a sub-9-lb/gal fluid that maintained its cohesiveness even when vigorously jetted into water or brine and would set to form a solid after sufficient fluid time to allow placement.

Needless to say, this complex composite composition required an unusual mixing protocol. The large volumes required for the target application added to the engineering, logistics and quality control obstacles that had to be tackled.

The end result of this focused research effort was the development of a novel composition that was applied via a novel mixing protocol. The cohesive system successfully sealed the flow channel it was designed for. As the development progressed, a wider range of utility was discovered for this novel composition. Several benefits of cohesiveness, density control, and hydration to form a solid seal were expanded to illustrate utility in other circumstances of well remediation.

This paper describes the development of the novel composition and mixing protocol. Potential for broader utility of the sealant remedial operations for petroleum wells is also presented.

Background and Theory

The first attribute addressed in the focused research was sealing. The material must start as a fluid to be pumped into the well, but it must then set to form a solid seal once reaching the flow channel. Two commonly-used oilfield materials with this attribute were considered: Portland cement and epoxy resin. Epoxy resin was cohesive, but prohibitively expensive for the volumes required. Additionally, environmental issues with handling the volumes required steered focus away from resin and onto the traditional sealant material. Thus, cement slurry became the starting point for the development.

The next property considered for the developing material was density. The fluid must be significantly lighter than saturated NaCl brine to migrate up to the targeted flow channel. The most common method of reducing density in a cement slurry is through addition of lighter materials to the design. Most often, the light-weight material is extra water. However, in this case excess water countered the composite's third performance attribute of cohesiveness to prevent dispersion. Therefore, hollow ceramic spheres (HCS) were chosen as the light-weight mechanism to minimize water concentration along with detrimental cohesiveness and strength development effects normally associated with reducing the cement to water ratio.

The cohesive property of the sealant required the most creative effort in the development process. Solids suspension of cement slurry is tenuous at best relying on weak surface charges, particle size distribution, and water to solids ratio to create a generally stable fluid. However, this fluid is easily miscible with other aqueous fluids, and the resulting mixture is highly unstable if the other aqueous fluid is not highly viscous.

The design approach to creating a cohesive sealant fluid was to gel the mix water. The approach is quite common in well drilling and completion as well as in oil production (enhanced oil recovery). In fact, the concept of gelation to create improved fluid cohesion is applied in almost all walks of life from paints to pharmaceuticals, to food. Mitov (2012) defines the basic functions of gelants used by chefs and futurist cooks as to contain, to stabilize, to coat, and to thicken.

These four functions were exactly what the developing sealant required. Working knowledge of gels used for hydraulic fracturing lead to focus on guar as the gelling agent. However, guar in the concentration required to produce a cohesive fluid is not normally added to a cement composition, since guar has a potent retardation effect on cement slurries. Additionally, gelation alone was found to be insufficient to provide cohesiveness, and crosslinking of the guar was required to provide sufficient structure. Guar pre-hydration at low pH then mixing of cement blend with gelled water produced sufficient base fluid gelation with low concentrations of guar to alleviate the retardation issue. The presence of HCS in the base gel-cement slurry proved fortunate when it came to crosslinking the base gel. Observance of base gel-cement-HCS blends revealed that the slurry thickened over a time of several hours ultimately taking on the three-dimensional structure of a cross-linked fluid. Further investigation revealed that the HCS consisting of borosilicate provide a boron source that is efficient enough to cross-link guar based linear gels. This boron concentration in the high-pH solution effectively cross-linked the system over time. The concentration was not sufficient in the time frame of this application, so a small concentration of borate cross-linker was added to the mix.

Once the cement composition demonstrated all the required performance criteria, a 9.5 lb/gal sealant system was floated onto a lab-prepared brine of saturated NaCl. The sealant initially floated and then sank to the bottom of the beaker. It was determined that the cohesive nature of the cement coupled with the low ionic strength of the cement fluid created osmotic pressure that drove ionized salt into the cement system. This influx of salt increased the sealant's density, and the sealant eventually settled to the bottom of the beaker. The salt influx did not disturb the cohesive structure of the sealant; it just made the sealant heavier. This problem was mitigated by lowering the sealant density (adding more water and beads) to less than 8.5 lb/gal. Then on contact with the brine, the sealant density remained lighter than the brine even after ionic strengths equilibrated.

Finally, blending, mixing, and placement protocols were developed, and large-scale laboratory mixing and placement tests were performed. Successful outcomes of these simulations reinforced the belief that the novel sealant was viable.

In yet an additional embodiment of the cohesive system, the cement has been replaced with sodium silicate to produce a stable lightweight plug. This cohesive settable sodium silicate formulation has been proven to be capable of being injected into a brine, float to the top of that brine, and then reform into a cohesive plug at the top of the brine. This can also be done with a sodium silicate solution heavier than the brine. This solution will sink to the bottom of the brine and form a cohesive plug. This is once again done by hydrating guar in water, adding sodium silicate, and then cross-linking the mixture with boron containing particulates to obtain a cohesive fluid capable of being injected or placed into another fluid and not dispersing.

Experimentation

In order to determine that the properties of the cohesive systems developed were adequate for their designed purpose, several non-standard tests were performed. The following sections contain descriptions of these test methods.

Mixability

The pre-gelled water being used as the mix fluid for the cement caused the slurry to become extremely thick if the composition was not correct, especially when the cross-link between the borate ions and gelled water started to form. Therefore, the first test that a composition had to pass was a simple mixability test. Since these slurries have to be mixed differently than standard cement, the traditional mixing procedures described by API (2010) were not used. Instead, the systems were kept on low shear for an extended period of time in order to allow the dry powder sufficient time to "wet." From there, different techniques were used to provide sufficient mixing energy to the slurry. The variations were dependent upon the design of the slurry. Mixability was determined visually and by the amount of time it took the slurry to "wet" on low shear.

Mixing HCS in the laboratory required special care. It is widely understood in the cementing industry that these "glass bubbles" cannot withstand the high shear normally applied to slurries during lab scale mixing of oilfield cements. The HCS will break or crack, thus losing their lightweight characteristics and raising the overall density of the system. To avoid this and apply enough mixing energy to the slurry, and extended period of mixing at low shear was used to mix low density designs of the cohesive fluid. The period of time chosen was five minutes once the blended dry components of the cement were "wet."

Slurries that did not require the use of HCS were allowed to mix on high shear for 35 seconds once the blended dry components had wetted. This technique was applied in the mixing of standard density slurries as well as higher density slurries.

Cohesiveness

The second test performed on the designs was developed to test the initial cohesiveness of the systems after they were mixed. This was done by taking the slurry immediately after it was mixed and, using a 60 ml wide-tip syringe, gently injecting the fluid into an Erlenmeyer flask filled with water or brine to determine if the system would hold together both through the force of the injection and as it matriculated through the fluid.

For lightweight slurries, 10 lb/gal NaCl brine was used. The slurries were injected a few inches below the surface and observations were made as to how the system matriculated through the brine to the surface and how well it self-healed into a floating cohesive plug. Any particulate settling was noted as well, as this was an indication that the system was not optimally cohesive.

Standard and high density systems were injected into water. It was again noted how the slurries both matriculated to the bottom of the flask and also how they re-formed into a cohesive mass. Particulate dispersion was also noted.

Conditioned Injection Test

The conditioned injection test is similar to the cohesive test, except the slurries were subjected to temperature and conditioning on an atmospheric consistometer. Following conditioning, the systems were injected, more rigorously this time, in the same manner as described in the previous section. This test was critical in that it assured that the systems could handle both an elevated temperature as well as the disturbance occurred during placement procedures. Temperature and conditioning times tested varied slightly, with the most common parameters being 110°F for 40 minutes.

Strength Development Testing

If a system passed mixing and both forms of the injection test, cube molds were then poured and placed in a bath to determine if the systems would set and develop strength. This was particularly important in lightweight slurries where the cement volume ratio was in some cases, too low for the system to develop strength. In addition, it was important for all density systems to develop strength in a timely manner. Typically, strength development was required to begin within the first 24 hours for standard and high density systems, and no more than 48 hours for low density systems.

Large Scale Testing

In addition to small scale lab analysis, large scale testing was performed on the lightweight system to provide proof of concept and determine any issues associated with larger scales of mixing. The test apparatus consisted of a 12 ft tall, 16 in diameter clear plastic pipe. This pipe was filled with 10 lb/gal NaCl brine. A ¾ in stainless steel tube was then placed inside this pipe, so that it ran centered through the clear plastic pipe. At the end of the ¾ in tube, a diverter was placed so that when flowed through, a liquid would be diverted perpendicular to the tube through two ports 180° apart from each other. Five gallons of the cohesive system were mixed and then pumped through the ¾ inch tubing. Observations were made as to how the slurry mixed, pumped, flowed through the diverter, and most importantly matriculated through the brine to the top of the liquid level in the 16 in plastic pipe. This test was performed only with potential candidates for use in the particular cavern application described earlier. Figure 1 shows an example of the setup and testing of the large scale pipe.

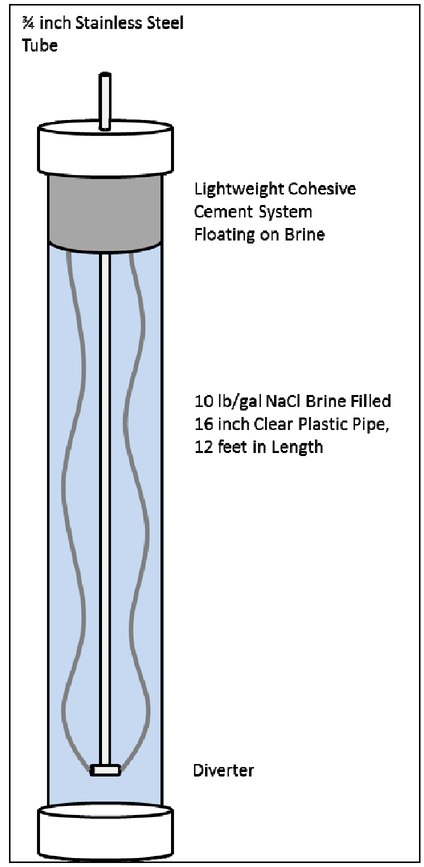

Figure 1: Large Scale Test Example

Discussion of Results

The following sections describe the general results of the testing performed to obtain the overall design parameters and limitations of the cohesive system at the time of this paper.

Basic Design and Mixing

The basic design of the cohesive system consists of four main components: water, cement, gelling agent, and borosilicate particulates. However, the order of addition and the method that this system is mixed is what makes it unique. To begin, the gelling agent is mixed into water in the same fashion that a linear gel for hydraulic fracturing would be prepared. This must be done so that the polymer can fully hydrate at a suitable pH. Cement slurries are extremely basic by nature and most gelling agents need a neutral to slightly acidic solution to fully hydrate or hydrate in an efficient amount of time.

The cement and HCS (or borosilicate particulates for normal density systems) are blended together to make a "dry blend" in the same fashion that a traditional cement system's dry components would be blended together. This blend is added to the gelled water and mixed similar to standard oilfield cements. The high pH provided by the cement now provides the optimum pH for cross-linking the guar with a boron source. The HCS or borosilicate particulates contain the source of boron. These particulates both provide the boron for cross-linking the gelling agent polymer chains and add structure to the system. Through this relationship a stable, cohesive cement system is created.

It is this marriage of technologies and techniques from hydraulic fracturing and oil field cementing that allows for this fluid to have its cohesive properties. In addition to the components listed earlier, standard oilfield cementing additives such as de-foamers, accelerators, and retarders can be added to the dry blend or the gelled water. Additional cross-linker can be added as well after the dry blend and gelled water have been mixed together if a stronger cross-link is needed.

Lightweight Designs

Lightweight testing was performed for a specific application. The application included the need for the system developed to be injected into a cavern filled with 10 lb/gal salt water brine, float to the top of that brine, reform into a plug, and quickly set to seal the top of the cavern. To accomplish this, a vast amount of testing was performed with a particular application targeted. The cohesive system developed performed exceptionally well. For this system, lightweight borosilicate glass bubbles were used. The final density of the cohesive system was 8.7 lb/gal, and the bubble concentration was 47% by weight of cement (%bwoc). These tests also included the use of solid sodium metasilicate, used as an accelerator, at a final concentration of 1%. The pre-hydrated gelling agent (guar) concentration was 26 lb/mgal of water. Below are the successful ranges of concentrations for the lightweight testing performed on this project.

Overall Density: 8.5-9.8 lb/gal
Bubble Concentration: 35-55 %bwoc
Guar: 15- 40 lb/mgal of water
SMS concentration: 1-6 %bwoc

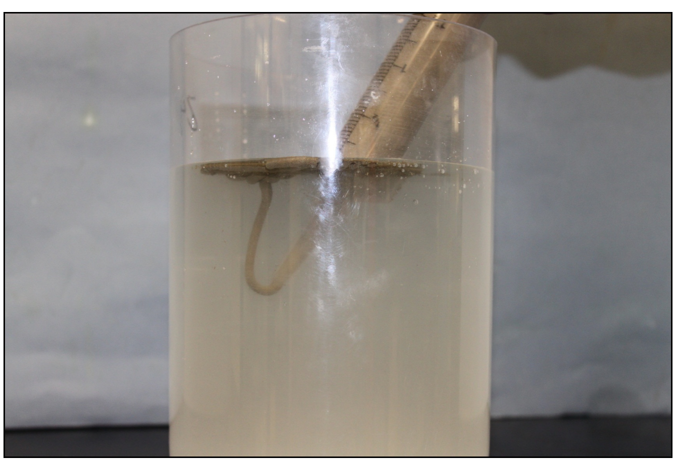

Figure 2: Injection Test of Lightweight Cohesive Design

Figure 2 shows a lightweight system being subjected to an injection test. Notice how the system "ropes" out of the syringe and rises to the surface of the brine. No settling or dispersion is occurring from either the injection stress or during matriculation. Figure 3 shows how the system transitioning from the "rope" form it reaches the surface at to a cohesive solid plug.

Figure 3: Lightweight Design Reforming Into a Single Cohesive Plug

Standard Density Designs

Once the specific lightweight system was used in the field, testing was performed at higher densities to determine additional application ranges of the cohesive system. Similar tests were performed, but at higher densities there is much less water in the system, and therefore much less gelling agent. Even at densities above 12 or 13 lb/gal, it was extremely difficult to design a cohesive system using materials available. Issues of mixability and overall stability of the cement were experienced. It was during this testing that it was discovered that the type of borosilicate particle and the size of borosilicate particle used is extremely important. It is critical that the borosilicate particles have a high boron content and that the majority of the particles be smaller than 74 µm. To date, the following ranges have been successfully tested:

Overall Density: 10-14 lb/gal
Borosilicate Concentration: 20-60 %bwoc
Guar: 15-40 lb/mgal of water

High Density Designs

To date, no high density systems have been successfully designed. This is due mostly to mixability issues (ultra-high initial viscosities). The mixability issues stem from the gelled water as well as the fact that high density slurries have a higher fraction of solids. Potential still exists with the addition of inert high density solids. It is predicted that densities up to 18 lb/gal can be obtained once slurry design and mixing procedures are optimized for high densities. 24 hour compressive strengths for all systems can be found in figure 4.

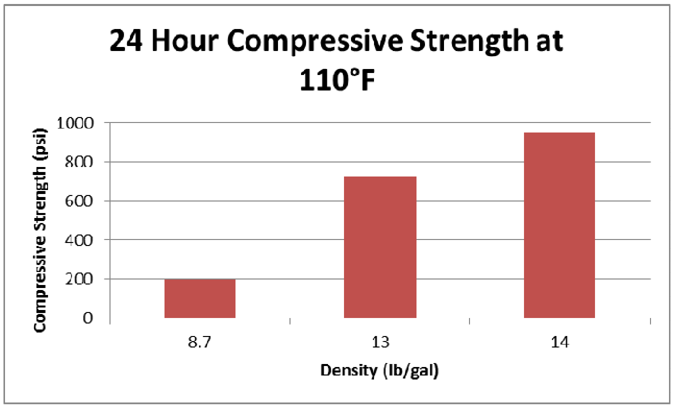

Figure 4: 24 Hour Compressive Strengths, 110°F

Importance of Boron Containing Particles

As mentioned before, it is crucially important that the system contain borosilicate particulates. This is due to several factors that allow the system to be cohesive. First, the particulates provide the boron source for cross-linking the gelling agent in the system. They also provide structure to the fluid by being solid inert particles. In lightweight slurries, the particulates are hollow glass spheres that reduce the overall density of the fluid.

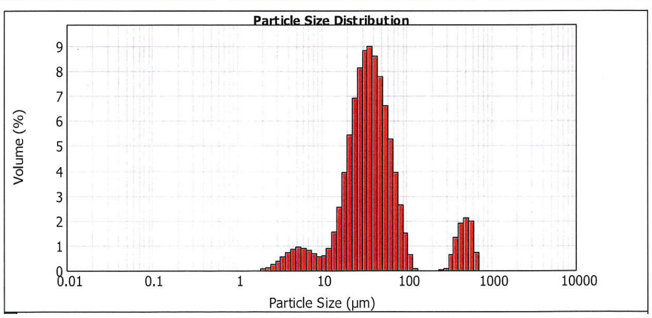

Figure 5: Particle Size Distribution Example of Successful Borosilicate Particulate

It is important to note that not all boron particulates will provide sufficient boron and structure. The size of the particulate is of extreme importance. If the particle is too large, not only will there be mixing issues but there will be undercrosss-linking due to insufficient coverage throughout the system. This will lead to a non-cohesive system that can settle or disperse when matriculating though another fluid. There needs to be enough particulates at a fairly small size so that they are distributed evenly throughout the fluid and can provide sufficient boron coverage. See Figure 5 for an example of a successful borosilicate's particle size distribution.

Special Considerations

Although several advantageous applications for this novel design have been identified, special considerations must be given to for the highest quality field placement scenario. Due to particulate matrix size and pre-gelation of the mix fluid, non-conventional mixing techniques must be used. During mixing, strict solids control monitoring must be employed within the mixing system to assure homogeneous cross-linking of the slurry. Vigneauz et.al. (2003) describe the process of mixing cement by solids fraction as opposed to density and the advantages and equipment associated for this type of mixing. Solids control monitoring devices are still a somewhat newer technology for cementing units and require special operator training for successful operation.

On additional piece of equipment that could be needed for field placement of this system is a cross-link fluid injection pump. Additional liquid cross-linker may be needed to achieve optimal cohesiveness in the system. This is accomplished by pumping cross-linker into the system between the downhole pump and the wellhead. Continuous monitoring of downhole pumping rate must be performed and the cross-link fluid injection rate must be varied to accommodate for changes in downhole rate during the job. Precise synchronization between pumps is required for optimum performance parameters. A setup similar to that in Figure 6 is required to successfully implement this system in the field.

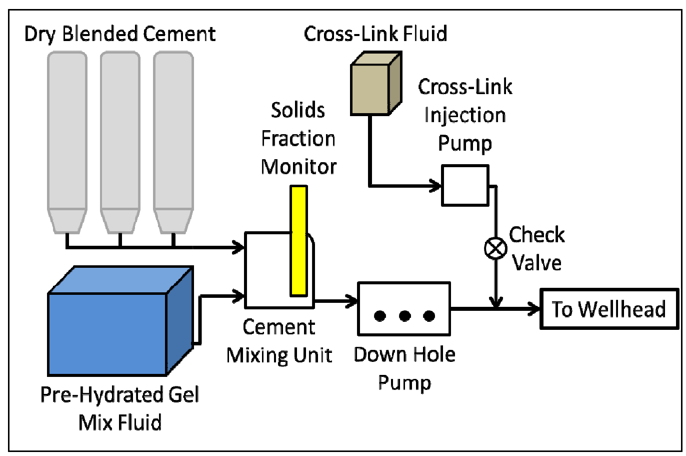

Figure 6: Mixing and Pumping Schematic for the Cohesive System.

Advantageous Properties

The advantageous properties of this cohesive system have already been alluded to in the previous sections, but need to be explained in greater detail. This system has properties of both a borate cross-linked guar fracturing fluid and an oilfield cement. Beyond the cohesive nature, another interesting characteristic of borate cross-linked systems is their ability to self-heal after experiencing high shear. Therefore, while the cohesive property provided by the cross-link allows the developed cohesive system to matriculate through other fluids without settling, it is the self-healing ability provided-by the cross-link to reform back into a singular fluid plug as opposed to either a "coiled rope" plug or individualized floating droplets. This is important because when the system does start to set, if it were not a single plug, there would be poor compressive strength and high permeability in the system. Once the plug is placed, the cohesive system will then set like a standard oilfield cement and develop significant compressive strength similar to that of a cement slurry of relatable density and design.

Potential Uses

Several potential uses for this system have been identified. These range from a number of different types of plugs to situations where anti-settling is a necessity. Of particular interest is its application as an extreme lightweight cement system. The cohesive system developed has already been proven to work as a lightweight system capable of matriculating through heavier fluids and setting as a plug at the top of that heavier fluid. However, this system can be used as a lightweight slurry for generic purposes as well. A common issue with lightweight slurries is their tendency to destabilize and settle. In addition, the cement to water ratio is so low that the compressive strength development is slow and very low. The cohesive system developed will not only be cohesive and anti-settling, but develop strength quickly and efficiently. The fact that there are HCS in the slurry allow for a higher cement to water ratio, meaning ultimately a higher compressive strength.

At standard densities, this system could be used as a plug or in any situation where settling would be an issue. One such use could be as a balanced plug. When placing a balanced plug, a sealant is placed on a heavier fluid at a particular interval that so that when the tubing being used to place the sealant us pulled out of the slurry, there is little to no disturbance of the liquid slurry. This is done in an effort to minimize settling and intermixing with other fluids in the well. With the cohesive system, there would be less possibility of settling or intermixing with the heavier fluid below.

For heavier densities, once again this system could be used to prevent settling of heavy solid particulates used to raise the density of the overall fluid or as a heavy plug. A scenario where this plug would be extremely effective is for plugging the top of packers. This is normally done because the packer has developed a leak for one reason or another and obviously cannot be serviced. Currently, resins or other types of weighted sealants are placed at the top of the wellbore and allowed to free fall through the fluid above the packer, where they will hopefully set and seal the area above the packer. Obviously, issues such as settling and dispersion can and frequently do occur while these sealants travel through the well fluid. This provides an ideal opportunity for the cohesive system as it could matriculate through the well fluid without dispersion, reform into a plug at the packer, and set to provide an effective seal.

Conclusions

1. The low density system was designed and applied successfully in the field.
2. The systems have been tested to be successful from a density range of 8.5 to 14 lb/gal.
3. The systems require some form of boron based solid particle, with the majority of the particles of its distribution being smaller than 74 µm.
4. There are no compatibility issues with other oilfield chemicals when used in their normal concentrations.
5. Higher density slurries could be successfully designed with additional testing and incorporation of high density inert particulates.

Acknowledgments

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Nomenclature

API	American Petroleum Institute
%BWOC	percent by weight of cement
ft	feet
HCS	hollow ceramic sphere
in	inches
lb/gal	pounds per gallon (density)
lb/mgal	pound/ per thousand gallons of water
mL	milliliters
NaCl	sodium chloride
SMS	sodium metasilicate

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