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Huntsman Mission

We are dedicated to giving our customers the finest quality and service available. Customers are valued partners who permit us to remain in business; we are privileged to serve their needs.

About Huntsman

Huntsman is a global manufacturer and marketer of differentiated chemicals. Its operating companies manufacture products for a variety of global industries, including chemicals, plastics, automotive, aviation, textiles, footwear, paints and coatings, construction, technology, agriculture, health care, detergent, personal care, furniture, appliances and packaging. Originally known for pioneering innovations in packaging and, later, for rapid and integrated growth in petrochemicals, Huntsman has approximately 11,000 employees and operates from multiple locations worldwide. The Company had 2009 revenues of approximately $8 billion. For more information about Huntsman, please visit the company’s website at www.huntsman.com.
POLYSIL® Series Coagulants

Huntsman coagulants are designed for use in the mining industry for the treatment of fine particles in aqueous suspension. Polyether coagulants are one of the few that are effective against the colloidal silica formed during the acid leaching of ores or slags containing silicates. POLYSIL® RM1250, POLYSIL® RM2050 and POLYSIL® RM3560 coagulants are liquid products that offer economic treatment of colloidal silica in a wide range of applications.

Natural silica as found in minerals has a low aqueous solubility. However when these minerals are digested in strong acids at elevated temperatures, large amounts of silicic acid is released. This can then polymerise in solution to form colloidal silica. This colloidal silica can be stable in solution at surprisingly high levels and for surprisingly long times. Under the right conditions it is possible for solutions containing over 3,000 ppm of silica to be stable for over twelve months at room temperature. The solubility of free silicic acid is about 160 ppm under these conditions, so the bulk of the silica is colloidal.

Colloidal silica can pass through a hydrometallurgy process without affecting any of the operations. However it can cause a number of problems. These include interfering with flocculation or crystallisation, and initiating crud formation in solvent extraction. In these cases coagulating the silica with POLYSIL® RM1250 or POLYSIL® RM2050 or POLYSIL® RM3560 coagulants can reduce or eliminate the problem.

Theory

Silica

Natural silica as found in minerals has a low aqueous solubility (for example, quartz about 7 ppm at room temperature in pure water). However when these minerals are digested in strong acids at elevated temperatures, large amounts of silicic acid is released. This can then polymerise in solution to form colloidal silica. This colloidal silica can be stable in solution at surprisingly high levels and for surprisingly long times. Stability depends on chemical and physical factors. Certain cations such as aluminium, manganese and molybdenum are very effective at stabilising colloidal silica, and pH is very important, with stability maximised at about pH 2. Physical factors include agitation and rate of cooling of digestion liquors. Under the right conditions it is possible for solutions containing over 3,000 ppm of silica to be stable for over twelve months at room temperature. The solubility of free silicic acid is about 160 ppm under these conditions, so the bulk of the silica is colloidal.

Silicic acid undergoes a complex series of interrelated condensations (Equation 1) and ionisations (Equation 2) depending on temperature, pH and impurities present:

\[
\text{Si(OH)}_4 + \text{Si(OH)}_4 \leftrightarrow \text{(HO)}_3\text{Si-O-Si(OH)}_3 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{(HO)}_3\text{Si-O-Si(OH)}_3 + \text{H}_2\text{O} \leftrightarrow \text{(HO)}_3\text{Si-O-Si(OH)}_2\text{O}^- + \text{H}_3\text{O}^+ \quad (2)
\]

Colloidal silica can pass through a hydrometallurgy process without affecting any of the operations. However it can cause a number of problems. These include acting as a protective colloid, interfering with crystallisation, and initiating crud formation in solvent extraction. In these cases coagulating the silica can reduce or eliminate the problem.

Note that it is usual in the mining industry to refer to any silica particle that is too small to be seen by eye as “silica in solution”. At what size a polymer is considered a particle is not clearly defined, so what is referred to here as colloidal silica may be referred to elsewhere as dissolved silica or silica in solution.
Coagulation differs from flocculation in a number of ways. Coagulants are relatively small molecules that modify the surfaces of the particles, weakening repulsive forces and allowing particles to stick together, while flocculants are generally molecules that are large enough to bridge the boundary layers between the particles. Because they modify the particle surface, coagulants can be structurally similar to dispersants, and in fact the same product that can act as coagulant in one situation can act as a dispersant in different circumstances. Polyether coagulants have a “lock and key” relationship with the surface of colloidal silica formed by the polymerisation of silicic acid. They have limited effectiveness against other materials.

Coagulation is an equilibrium process. With flocculation, order of addition, rate of addition and mixing all make a difference to the flocs formed, and flocs have limited lifetimes. With coagulation it is only necessary to achieve good mixing, and coagulates will then form as Brownian motion pushes the particles into each other. In real systems, this process is complete within seconds.

POLYSIL® RM1250 coagulant is effective against particles down to about 20 nm or 0.02 microns. Once coagulates are formed, they rapidly cement themselves together so that the larger particles become permanent.

Protective Colloids

When flocculating acid digestion slurries, silica can act as a protective colloid. A colloid is called a protective colloid if it interferes with or prevents the settling or flocculation of larger gangue particles present with that colloid. Colloidal silica particles carry a weak negative charge. These charged particles repel each other, so spread themselves as far as possible from each other in solution. This acts like a net holding other particles in suspension that would otherwise settle. This effect is clearly seen in a sample of digestion liquor before or after flocculation.

As most flocculants do not adhere well to silica surfaces, they are difficult to flocculate using conventional flocculants. The silica particles then resist the growth of other gangue flocs by a process related to Donnan exclusion. That is, they do not want to be trapped in pores within the flocs. The result can be slurries that are difficult to flocculate, have high flocculant demand, and give “rubbery” flocs with low settled densities.

To understand how a relatively small amount of silica can interfere with the flocculation of a large amount of other solids it is useful to look at the number and surface area of the silica particles present. If we assume the colloidal silica to have an average particle diameter of 0.01 microns, and the gangue minerals 3.5 microns, and there is 5 % by weight of gangue and only 260 ppm silica, there are still $10^5$ times as many silica particles as gangue particles in any volume of slurry.

If a flocculant, such as a weakly cationic flocculant, is used that does bind to colloidal silica, the high surface area of the silica consumes large amounts of flocculant. In the above example, the surface area of the silica is equal to the surface area of gangue.

Coagulating the silica increases the particle size, consequently decreasing the number and area of silica particles. This reduces their effect, and can also make them easier to remove during flocculation.
Symptoms to look for where silica may be acting as a protective colloid are high flocculant demand, low floc density and the presence of “floaties” in the settled supernatant. Where the floc is filtered, filterability is poor. If silica is the cause, coagulation of the silica prior to flocculation will be effective. Typically there can be a reduction of up to 50% in flocculant demand, and marked improvement in supernatant clarity. A clear “break” should be seen between the floc layer and the supernatant as the flocs settle. Underflow density and/or filterability should improve markedly.

**Crystallisation and Scale**

This is closely related to flocculation. The high surface area of colloidal silica allows it to adsorb on growing crystals, blocking further growth. This results in a large number of poorly formed crystals rather than a small number of large, well-formed crystals. If the silica sticks to a solid surface and to the growing crystal, it can act as the anchor point for the growth of scale.

**Solvent Extraction**

It is in solvent extraction that silica can have the most dramatic effect. Here if the silica particles have the right size and the correct contact angle, they stabilise the emulsion formed in the mixers. These are the so-called Pickering emulsions [Figure 1].

When Pickering emulsions form, it is more likely that they will be aqueous continuous, but with a low volume fraction of water. The colloidal particles allow the water to drain out to a point, then stabilise the water film at a thickness close to the particle diameter. This frees water to the rest of the system making it more likely that it becomes aqueous continuous and so on. This is why siliceous crud can cause mixers to flip. It is also why less crud is formed if the mixer is run organic continuous, as crud can only form in areas that are locally aqueous continuous.

Coagulation of the silica is twice beneficial. Coagulated silica is easier to remove from solution, and any remaining silica particles are too large to stabilise crud.

Note that silica is not necessarily the largest mineral component in a siliceous crud. Once the crud forms it is strong enough to trap and collect any other particles in suspension. By the same arguments as used above, the mass of a small number of these large particles can easily exceed the mass of the silica stabilising the crud.
Figure 1:
Pickering Emulsion – Oil-in-Water Stabilised by Silica Particles

Figure 2:
Importance of Contact Angle and Particle Size

A smaller particle will need a larger contact angle ($\theta_2 > \theta_1$) to be stable in the same aqueous film as the larger particle. Alternatively, with the same contact angle it will stabilise a thinner film. If the film is too thick the emulsion will be mechanically unstable; if too thin it the films will tend to rupture from Brownian motion.
Some Case Notes

Case 1
A mixed oxide and sulphide ore is digested with hot sulphuric acid to release copper and uranium. The residue is washed and clarified in classical high rate thickener/clarifier system backed up with sand filters. The clarified liquor is passed through copper and uranium solvent extraction. No unusual problems are observed in copper Sx, but in uranium Sx large amounts of stable crud are formed.

In this case the silica particles are between 0.05 and 0.2 microns in diameter, ideal for forming crud. However their surface is too hydrophilic to adsorb onto the organic phase in copper Sx. In the USx the amine extractant binds to the negative silica surface making it more hydrophobic so that it can stabilise crud.

The answer was to coagulate silica prior to final flocculation in the clarifier. The coagulated silica particles were large enough to be trapped in the flocs or removed in the sand filter. The coagulant specifically targets the silica that stabilises the crud.

Case 2
Chalcocite is digested in an autoclave with sulphuric acid. The product is difficult to flocculate, and the flocs are difficult to remove by settling or filtration, and there is a high level of suspended solids.

The solution was to pass the digested pulp through a hydro-classifier that separated fine particles from the bulk of the solids. The underflow could then be readily filtered. The overflow was treated with POLYSIL® RM1250 coagulant and then flocculated. These flocs could then be removed by conventional means, to leave a supernatant with less than three parts per million of suspended solids.

Case 3
Uranium is released from an ore by a combination of oxidation and sulphuric acid digestion, and the uranium recovered by solvent extraction. Colloidal silica levels are typically 2,500 to 3,000 ppm, but there is no formation of siliceous crud.

The silica particles are presumably too small to stabilise crud, or have the wrong surface chemistry to adsorb the amine extractant. Ions such as manganese IV (or even manganese III stabilised by adsorption on the silica) reverse the surface charge on the silica so that the amine does not adsorb.

Case 4
An oxide ore is dissolved in autoclaves with sulphuric acid, and the solution partially neutralised with lime and clarified before the solution is sent to solvent extraction. The gypsum formed is very fine and voluminous, and the resulting slurry is difficult to flocculate.

Silica was adsorbing on the surface of the gypsum crystals, preventing further growth. Treatment with POLYSIL® RM1250 coagulant during neutralisation improved crystal size, reduced flocculant demand, and improved supernatant clarity.
POLYSIL® RM1250 Reagent

**DESCRIPTION**
An aqueous solution of a high molecular weight polyglycol.

**SPECIFICATION**
- Appearance @ 20°C: Clear, viscous liquid
- Water content, %w/w: 49 - 51
- pH, 5% aqueous solution: 4.5 - 7.5

**TYPICAL PROPERTIES**
- Specific gravity @ 20°C: 1.09
- Viscosity, cP @ 20°C: 400

**SOLUBILITY**
POLYSIL® RM1250 reagent is readily miscible with water, simple alcohols and esters, glycol ethers and other polyglycols. The base polyglycol is also soluble in a wide range of solvents but the presence of water in POLYSIL® RM1250 reagent obscures this effect.
Product Data Sheet

POLYSIL® RM2050 Reagent

Document ID: SUR3317105
Revision No: 0

DESCRIPTION
A broad range, polyether based coagulant.

SPECIFICATION
Appearance @ 25°C Clear, light straw to brown, viscous liquid
Viscosity, cP @ 25°C 80 - 120
pH, 1% aqueous solution 5.0 - 8.0
Solids content, %w/w 28 - 30

TYPICAL PROPERTIES
Specific gravity @ 20°C 1.050
Pour point, °C < 0

SOLUBILITY
Soluble in water in all proportions at all temperatures. Insoluble in organic solvents.

USES
Coagulant for use in the mining and related industries for the coagulation of silica and other fine particles in solutions of all pH values.

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POLYSIL® RM3560 Reagent

Document ID: SUR0867413
Revision No: 0

DESCRIPTION
A broad range, polyether based coagulant.

SPECIFICATION
- Appearance @ 25°C: Clear, light straw to brown, viscous liquid
- Viscosity, cP @ 20°C: 380
- pH, 1% aqueous solution: 8.0 – 11.0
- Water content, %w/w: 44 - 46

TYPICAL PROPERTIES
- Specific gravity @ 20°C: 1.08
- Pour point, °C: < 0

SOLUBILITY
POLYSIL® RM3560 coagulant is soluble in water in all proportions. It is generally not miscible with organic solvents.

USES
POLYSIL® RM3560 coagulant is designed for use in the mining and related industries for the coagulation of silica and other fine particles in solutions of all pH values.

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