THE APPLICATION OF POLYSIL® COAGULANTS TO REDUCE CRUD FORMATION BY CONTROLLING COLLOIDAL SILICA

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ABSTRACT

The problem of crud in solvent extraction is well known and can be a major handicap and operational issue. Colloidal silica can cause a number of problems including interfering with flocculation, initiating crud formation in solvent extraction (SX), decreasing SX extraction kinetics and increasing SX phase disengagement times. Flocculation can be utilized to remove some of the troublesome particulates but colloidal silica does not flocculate well and presents a different problem requiring innovative chemistry to solve. Coagulants can assist by facilitating the removal of this colloidal silica by promoting the agglomeration of the particles to a size which can be more readily settled or flocculated in solid/liquid separations. This is achieved when the coagulants bind to the surfaces, displacing water and destabilizing the colloids, whereupon they bind to each other which facilitate their amenability to conventional flocculation.

KEYWORDS

Colloidal silica, crud, Solvent Extraction, Coagulant, POLYSIL®, XXVIII International Mineral Processing Congress
INTRODUCTION

Silicate minerals are abundant in the upper layers of the Earth’s crust, and there are few mineral deposits without significant levels of gangue silicates. Silicate minerals include the pure silicas, such as quartz and other silicate containing minerals such as clays, chlorites, feldspars, as well a vast number of less common silicates.

During the acid leaching of ores, two types of fine silica particles are released in solution from the dissolution of the host mineral. The first consists of partly depleted silicates, and the second is colloidal silica, which forms in solution. It is this second type which has the potential to cause crud formation as well as poor solution clarities, slow filter rates and excessive flocculant usage (Figure 1).

Figure 1 – Colloidal silica is formed in the leaching stages on the left and can cause issues in clarification, filtration and solvent extractions

Formation of Colloidal Silica

Acids do not readily attack acidic silicates, such as quartz. Silicates are attacked by the dissolution of the metals present in the structure. Many basic silicate minerals contain metal ions, typically sodium, potassium, iron, magnesium and aluminum. These are extracted during leaching, causing the three dimensional silicate structures to fall apart and essentially depolymerize to silicic acid (Figure 2). The rate of acid attack will vary significantly from mineral to mineral, but even within one class of minerals the rate will vary depending on particle size and crystallinity.

Figure 2 – Acid leaching of metals from the clay crystalline structure causes the remaining structure to fall apart

Silica in solution starts life as silicic acid and then reacts along two separate pathways:

Dissociation
\[ \text{Si(OH)}_4 \leftrightarrow \text{SiO}^{-} \cdot \text{(OH)}_3^- + \text{H}_3\text{O}^+ \]

Polymerization
\[ 2 \text{Si(OH)}_4 \leftrightarrow (\text{OH})_3^- \cdot \text{Si-O-Si} \cdot (\text{OH})_3 + \text{H}_2\text{O} \]
The solubility limit for silicic acid is in acidic solutions at pH 2 is approximately 150 ppm (Iler, 1979). Above this concentration, silicic acid polymerizes to form colloidal particles, precipitates, or a gel (Queneau, 1986). In hydrometallurgy circuits, this process can be chaotic and can be very fast. This growth results in a wide range of particle sizes, as well as precipitated silica and in special cases, silica gel. The polymerization behavior of silica, in acid and basic conditions is shown schematically in Figure 3.

Figure 3 – Polymerization behavior of silica. In basic solution (B); in acidic solution or in the presence of flocculating salts (A). From Iler (1979).

**Coagulation of Colloidal Silica**

Flocculants, often polymers, are commonly used for settling fine particles. However, the removal of colloidal silica requires a coagulant to grow and settle these particles as flocculants are poor at settling particles in the sub-micron range. 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.

Huntsman’s POLYSIL® polyether coagulants have a “lock and key” relationship with the surface of colloidal silica formed by the polymerization of silicic acid. The coagulants are effective against particles down to about 20 nm or 0.02 µm. Once coagulates are formed, they rapidly cement themselves together so that the larger particles become permanent.

The use of POLYSIL® coagulants in hydrometallurgy plants where colloidal silica is present in leach liquors has been shown to improve solvent extraction performance (Thomas, 1996). This can be done by coagulating the colloidal silica with a coagulant; colloidal silica particles then grow in size to the point where they can be flocculated and removed from leach liquors. The coagulation and removal of these colloidal particles significantly improve solution clarity.

By treating leach liquors before they undergo solvent extraction, emulsion events associated with colloidal silica such as continuity flipping and crud formation can be significantly reduced, thus reducing costly organic losses.
COLLARIFICATION AND FLOCCULATION

Colloidal silica can have a dramatic effect on both flocculant demand, and the clarification of Pregnant Liquors (PL), in essence, the leachate. The mechanism by which colloidal silica blocks clarification is called the protective colloid effect. Each of the silica particles is stabilized by two or more layers of hydrogen bonded water.

For example, if there is 0.5 g/L of silica in solution, about 0.2 g/L will be colloidal silica with an average diameter of 0.05 µm, then there will be eight hundred trillion (8 × 10^{14}) particles per liter. This will far exceed the number of all other particles put together, even though silica is a minor component by mass. These particles are separated by less than 1.5 µm from each other. This means that other, larger, fine particles are supported by the network of colloidal silica particles, and have to “force” their way through in order to settle, and so are held in suspension (Figure 4).

![Figure 4 – Colloidal silica particles can form a block network that can slow settling and suspend larger particles even when flocculant molecules are used](image)

Combined with the fact that many flocculants do not bind to colloidal silica, there exists a second mechanism, the physical blocking of the flocculant polymer chains by silica particles that prevents them finding and bridging gangue particles. While there is not a lot of direct scientific evidence for either of these effects, they are useful explanations for what is observed in practice, the presence of colloidal silica in solution can greatly increase flocculant demand and still results in cloudy PL with high total suspended solids.

The number of fine colloidal particles can be reduced by coagulation so that particle size is increased and total surface area is reduced. These coagulated colloidal silica particles increase in size to where they can themselves be flocculated and removed (Figure 5).
Coagulation of colloidal silica with a coagulant will increase particle size into the flocculation range and reduce the overall number of colloidal particles. This can make a clear solution go milky, as particles grow into the visible range. An example of this in Figure 6 shows a clarification test on a copper leach stream feed to a clarifier containing 700 ppm silica. Treatment with 50 ppm of POLYSIL® RM1250 coagulant reduced silica to 300 ppm, thus removing the blocking network of colloidal particles to give better settling and cleaner liquor.

For Solvent Extraction (SX), a Total Suspended Solids (TSS) concentration of less than 20 ppm is considered ideal, although many plants operate with average TSS figures above 40 ppm. The cost of TSS in the feed to an SX circuit is high. Generally, SX, including all designs of mixer settlers and pulsed columns, is efficient at removing solids. This means that at a minimum, every cubic meter of PL with 20 ppm solids generates 40 grams of sludge, since the sludge also contains organic and aqueous entrainment. This is a direct cost in terms of lost reagent and the physical removal of sludge from equipment. Aqueous entrainment can have up to 100 parts of organic to every part of fine solids, especially if the solids are colloidal silica.
Colloidal silica can stabilize the water film at a thickness close to the particle diameter. The small particles stabilize the film and sit in the corners, preventing the oil droplets from moving (Figure 7). This can result in a semi-rigid structure with the consistency of beaten egg whites, otherwise known as Pickering emulsions (Komura, 2006).

Figure 7 – Emulsion of oil in water stabilized by the colloidal silica particles at the interfaces

Less crud is generally formed in a mixer run in organic continuous (OC) (Readett, 1995), as crud can only form in areas that are locally aqueous continuous (AC). Silica generally favors AC, and can cause flipping from OC to AC on the Plant. This is because if a zone of AC is formed, its lifetime is greater and so can build up at the expense of OC regions.

Phase continuity is important and can usually be determined by observing the interface. In organic continuous the aqueous droplets are falling out of the organic phase, and vice versa. Organic continuous will have a ragged upper surface and a flat lower surface. Aqueous continuous (AQ) will have a ragged lower surface and a flat upper surface. Aqueous continuous phase disengagement times are usually much longer than organic continuous.

CRUD

Colloidal silica can lead to emulsification, crud formation, and high entrainment losses in SX. On the other hand it can behave like just another anionic species in solution and pass right through. A good light microscope will show the crud structure, and the droplets of organic should be clearly visible at high magnification; crud is almost always aqueous continuous. A scanning electron microscope is needed to look at the solids (Figure 8). Crud collects suspended solids very efficiently, and large particles contribute to mass. The fact that hematite, for example, is the major component of a crud solid sample does not mean that it is a hematite crud. If 5% of those solids are pure silica, then it is very likely that it is a silica crud.
Tertiary amine extractants are particularly susceptible to emulsification as the amine can bind to silica surfaces (Kordosky, 2007) thus making colloidal silica particles partially hydrophobic. This brings silica to the interface and causes emulsion (Figure 9). This then becomes a collecting point to trap any solids in the PL feed to SX. It can also be carried downstream to washing and stripping stages where the silica may precipitate, and either trigger crud formation or add to crud formation.

**OPERATING EXAMPLES**

BHP Billiton Olympic Dam reduced suspended solids to below 50 ppm by the addition of a silica coagulant. The removal of colloidal silica and reduction in solids help to reduce crud in the solvent extraction circuit. The process consists of flotation tailings being leached in sulphuric acid to dissolve uranium and any remaining copper. The solids are separated from the pregnant solution by a counter-
current decantation. The pregnant solution passes through a clarification stage in order to remove colloidal silica (Thomas, 1996).

Nyrstar Port Pirie uses POLYSIL® coagulant from Huntsman in their copper leach plant. This plant processes copper-lead matte which is a byproduct from the lead blast furnace. Coagulant is added to the second stage leach (or high acid repulp) mixing tank. The re-pulp reactor is an aggressive leach, it has long residence times and high acid and chloride levels. The POLYSIL® coagulant aids in the colloidal silica control (Dudley, 1996).

In the modernized Pasminco Electrolytic Zinc calcine leaching circuit, a silica coagulant was key and the most cost effective means of solving their colloidal silica problem. Colloidal silica was leading to low density thickener underflows, containing less than 200 g/L solids which increased recycle flows. The use of a coagulant for colloidal silica in the jarosite precipitation stage enabled the thickener underflow densities to increase to over 400 g solids/L, which increased throughput of the plant and product quality (Kershaw, 1995).

Clarification

The following tests were carried out during a period of processing where a high concentration of problematic chlorite gangue mineral was present in the feed. Chlorite from previous operating experience was associated with increases in silica concentration in the pregnant liquor solution (PLS) leading to emulsion and reduced throughput through the SX circuit.

Clarification was simulated by adding coagulant, adding seeding solids and adding flocculent with mixing at each addition. The solids were allowed to settle from solution over 4 hours before sampling for assay and phase disengagement time (PDT). Silica was assayed via inductively coupled plasma mass spectrometry (ICP-MS) to determine total silica (Figure 10).

![Figure 10 – Dose response curve for coagulant addition versus silica concentration in the PLS](image)

Turbidity was measured on the solutions once settled and a clear improvement in solution clarity could be seen once a dose of 50 g/m³ of POLYSIL® RM1250 coagulant was added (Figure 10).
Dose response testing was carried out over a number of days and as the silica concentration increased with chlorite content, so did the required dose of POLYIL® coagulant (Figure 12). Optimum dose typically lies in the 40 to 80 mg/L range, though dose response curves need to be carried out to become familiar with the behavior of a specific system and in order to estimate the dose that will be most reliable and effective. Optimizing the dose involves working out the balance between the cost of overdosing and the cost of under-dosing. Under dosing can result in lost product, lost SX reagent and down time.

As colloidal silica cannot be measured directly, it is measured by measuring total silica and a filtered sample for silica. The filtered sample is passed through a 0.1μm syringe filter to remove colloidal particles therefore allowing colloidal silica to be calculated by difference. Silica concentrations are best determined via ICP.
Phase Disengagement Testing

Using freshly made up organic and synthetic aqueous phases will give the best (shortest) possible PDT. A good PDT protocol for a one liter sample is typically between 30 and 60 s. Filtering the PLS through a fine (0.1 µm) membrane filter before adding it to the organic will show whether fine particles are responsible for a long PDT. Adding 50 ppm POLYSIL® coagulant to the unfiltered Plant aqueous phase and mixing for 90 seconds before adding to the organic will show whether colloidal silica is responsible for a long PDT.

The PLS from clarification tests were run though copper (Figure 13) solvent extraction to determine phase disengagement times. Organic continuous tests for both copper were relatively fast. Once these were flipped to aqueous continuous, the untreated PLS still containing about 0.7 g/L of silica gave very slow phase disengagement and heavy emulsification between the organic and aqueous phases. PLS treated with POLYSIL® coagulant was seen to give fast and clean phase disengagement with no emulsion present at the interface.

![Figure 6 – Copper aqueous continuous solvent extraction phase break times](image)

CONCLUSIONS

The use of coagulants to precipitate fine colloidal silica particles from leach liquors has been shown to be an effective means of improving processing outcomes in hydrometallurgy plants. By coagulating colloidal silica, these particles can be grown in size to the point where they can be flocculated and removed from leach liquors. The removal of these fine colloidal particles can reduce flocculent demand, enhance settling rates and improve TSS and solution clarity of overflow liquors from CCD / clarifiers reporting to solvent extraction. The removal of colloidal silica from leach liquor going to SX has also been shown to improve performance, especially where tertiary amine extractants are used. By treating leach liquors before reporting to solvent extraction, emulsion events associated with colloidal silica such as crud formation and continuity flipping can be significantly reduced, thus reducing costly organic losses.

REFERENCES


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