Ceramic proppant acid dissolution – when does it matter for your well, and why

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Sand and man-made ceramics are the two primary types of proppants the hydraulic fracturing industry employs. Selecting the right proppant for a well focuses on the mechanical stability of proppants under down hole (application) conditions which then ensures proppant is able to deliver desired fracture conductivity. The chemical stability of proppants is also an important selection factor. All types of proppants are typically very chemically robust and do not interact with fracturing or producing fluids. However, certain types of acids or producing fluids can damage proppant integrity and compromise their performance. This is particularly important consideration during selection of ceramic proppants as they are typically the proppant of choice for deepest wells with harshest corrosion condition. Knowing when an issue might occur takes a deep look into the structure of proppants, their affinity towards certain acids and application conditions.

What is really inside ceramic proppants?

The composition and microstructure of any product determines its chemical stability. Ceramic proppants are typically produced from either bauxite or clay raw materials. Each of these minerals occupies a unique regime in the Al₂O₃-SiO₂ system: bauxite minerals contain more than 70 wt% Al₂O₃ while clay minerals contain between 40 and 60 wt% of Al₂O₃. Proppants made from these minerals consist of three major phases: corundum, mullite, and crystalline or amorphous silica. Alkali silicate glassy phases and different iron aluminate phases can also be present in bauxite based proppants (1).

While all above mentioned phases are chemically robust their do show affinity towards some of industries most aggressive fluids – HCl (hydrochloric) and HF(hydrofluoric) acid. This affinity of a crystalline form to react with acid in physical contact is defined as acid solubility. Silica, a key ingredient in clay based materials, has a known solubility in HF acid (2) (3). Solubility kinetics of corundum, mullite, and glass in HF acid and combination solutions of HF and HCl acid are also well documented in literature. Most of these materials are relatively inert towards attack of HCl acid, but only corundum is relatively inert toward attack of HF acid (4). Amorphous silicate compounds, such as amorphous SiO₂ or the more general silicate glasses, are soluble in HF acid (3). While crystalline forms of SiO₂ exhibit dissolution rates that are 2 to 3 times slower than those of their amorphous compounds, silicate alumina glasses can exhibit dissolution rates that are 2 to 10 times faster than amorphous silica. Dissolution of mullite in HF acid is lower than crystalline SiO₂ but generally higher than that of corundum (4).

It is not about just how much dissolves, but what dissolves.

For gravel packing applications, the solubility of proppants in acidizing fluids is an important factor affecting product selection. The test for acid solubility recommended by API (ISO 13503-2) (5) determines the weight loss of proppant after 30 minutes of exposure in an acidizing environment of a 12:3 HCl:HF solution (mud acid). To many in the industry, the measured weight loss value helps
determine the suitability of a proppant that can come into contact with acid. For ceramic proppant selection industry typically considers 7% as a maximum acceptable solubility limit. Published studies (1) show that while all types of ceramic proppants show acid solubility lower than 7% proppants their mechanical performance is not proportional to measured acid solubility number. Bauxite based VersaProp proppants post acid treatment show no change in their mechanical performance while clay based Economy LWP proppants experience significant degradation (increase in the amount of fines generated during crush test, Figure 1).

![Figure 1](image.png)

**Figure 1.** Crush Resistance results of VersaProp and Economy-LWP specimens as a function of time of mud acid exposure at a pressure of 8,000 psi. Post acidizing bauxite proppants (VersaProp) show more robust mechanical stability (lower % of crushed particles under stress) than Economy-LWP proppants.

Additionally, mechanical compression tests show higher compaction of acid treated Economy-LWP proppants than that seen in VersaProp proppants (Figure 2). This acid induced proppant Economy-LWP “softening” leads to decrease in the size of pore throat openings and direct reduction in proppant pack permeability.

The reason behind this phenomena lies in the microstructure of acid treated samples. Microstructures of acidized samples of VersaProp, Figure 2, show that the acid etches inter-crystalline, silica rich, matter without effecting the mullite-corundum structural matrix, permitting the VersaProp strength to remain intact. Conversely, post acidizing microstructure of Economy-LWP, reveals a much different “skeleton” structure with small needle like crystallites and presence of surface pits known to create high stress.
concentration regions that promote mechanical failure of the proppant and an increase in fines generation at lower closure stresses.

Figure 2. Compaction of VersaProp and Economy-LWP specimens at 8,000 psi before and after exposure to mud acid. Post acid treatment Economy-LWP proppants experience a high pack compaction due to “acid softening” effects.
Figure 3. Scanning electron micrographs of VersaProp proppants surface before and after exposure to mud acid. In VersaProp proppants acid dissolves with glassy phase but proppant crystalline skeleton remains intact ensuring strength of proppant is retained after acid treatment.
Figure 4. Scanning electron micrographs of Economy-LWP proppants surface before and after exposure to acid. In clay based proppants acid dissolves both glassy phase and crystalline silica phases, and creates surface pits.

Going beyond gravel pack: Combined acid and hydraulic fracturing in unconventionals.

While originally developed more than 30 year ago, combined acid and proppant fracturing (CAPF) is showing promise in stimulation of shale formations (6) (7). CAPF is different than historical acidizing stimulation techniques such as matrix acidizing and acid fracturing. Matrix acidizing improves permeability of the near well bore rock by dissolution of sediments and mud solids. On the other hand in acid fracturing acid is pumped as a fracturing fluid and is used to both physically fracture the rock and chemically dissolve sediments, thereby creating flow channels. Neither of those techniques utilizes proppants. During CAPF acid is injected as a pre-flush treatment, but also during fracturing where acid...
increases shale formation porosity and recovery factors, while proppants provide mechanical stability of induced fractures. This approach is known to be most successful in carbonate rich formations, such as Eagle Ford. Analysis of public data shows that more than 75% of all completed wells in Eagle Ford used acid during completion (Figure 4). However, acid use is also on the rise in other unconventional plays such as Bakken Figure 4). The use of acid in Bakken has increased several fold and today close to 45% of the wells completed in that area use acid as part of their completion process.

Figure 4. Analysis of public chemical disclosure data shows acid use in Eagle Ford and Bakken
Industry today faces a challenge as current API testing protocols cannot be used to evaluate effect of acid on ceramic proppant in unconventional applications. First, CAPF uses HCl acid solution and not a mud acid solution specified in the API test. Secondly, testing conditions of 150 degF is not appropriate since proppant will see acid at temperatures in access of 250 degF. Most importantly, current API acid solubility procedure should not be used as it gives no indication of acid corrosion induced loss of mechanical strength in proppants. Development and implementation of appropriate testing method is critical as presence of phenomena such as acid softening of Economy-LWP proppants can be very detrimental in CAPF completions, as it will have a direct effect on the retained fracture geometry.

While data on HCl acid dissolution of Economy-LWP proppants is currently not available, performance of bauxite based VersaProp proppants has been measured (Figure 5) and shows that even at extreme conditions (300 degF, elevated pressure) dissolution rate of bauxite based ceramics is minimal.

![Figure 5. 10%HCl acid dissolution results for VersaProp using a modified API procedure and a high temperature high pressure See Thru Cell. See Thru Cell testing conditions closely mimic those expected in unconventional shale plays](image)

Proppants interaction with producing fluids

Crude oil and natural gas fluids often carry various inherently corrosive substances, such as carbon dioxide (CO$_2$), hydrogen sulfide (H$_2$S), and free water (8). These impurities increase operational safety risks and can be detrimental to production, both in terms of equipment damage and permeability impairment caused by scale deposition. Furthermore, the impurities (CO$_2$, H$_2$S, and free water) can be detrimental to oil/natural gas production in terms of permeability and productivity loss caused by scale deposition. Iron sulfide (FeS) scale occurs when H$_2$S comes in contact with dissolved iron ions. FeS scale deposition caused by a reaction between H$_2$S and steel pipeline walls and/or iron bearing core materials is a known industry problem. Today the most common approach used to minimize FeS scale deposition
risk is addition of $H_2S$ scavengers, as well as, minimization and control of the use of iron bearing compounds during well completion.

Ceramic proppants can also contain iron in various amounts, typically 1-10%. Recently published study investigated if iron present in the proppants can contribute to scale formation in sour wells (8). Analytical analysis of three different types of North America bauxite based proppants, and shale core showed that dissolution kinetics of shale core and proppant samples are very different. Iron containing compounds in all ceramic proppants tested in this study demonstrate high stability in aqueous $H_2S$ acid solution. None of the analytical techniques used are able to detect dissolution of iron or FeS precipitation. This is not a surprising result as iron in bauxite based ceramic proppants originating from North America contains pseudobrookite. Pseudobrookite has very low affinity towards $H_2S$. On the other hand, the iron bearing shale core sample shows high reactivity with aqueous $H_2S$ resulting in both dissolution of shale core as well as precipitation of FeS scale. Since the dissolution of Fe containing minerals in shale is much faster than that seen for proppants, any scale formation observed during the lifetime of the well will have primary source of the Fe as originating from either formation rock or steel piping. Results shown in this study suggest that bauxite based proppants containing pseudobrookite are not a significant contributor to FeS scale formation and can therefore be safely used in sour wells.

![X-ray diffraction patterns of iron containing proppant and shale core sample before and after exposure to aqueous $H_2S$. Iron containing shale samples show high reactivity towards $H_2S$ while iron containing ceramic proppants remain unchanged.](image)

Figure 6. **Figure X-ray diffraction patterns of iron containing proppant and shale core sample before and after exposure to aqueous $H_2S$. Iron containing shale samples show high reactivity towards $H_2S$ while iron containing ceramic proppants remain unchanged.** Labels on the XRD pattern refer to muscovite ($Mu$), albite ($Al$), amesite ($Am$), quartz ($Q$), calcium carbonate ($Ca$), iron oxide ($Fe$), and pyrite ($Py$) respectively, react.
Bibliography


