Experimental study of the effect of hydrothermal alteration on proppant brittleness

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ABSTRACT

A major challenge to using proppant in geothermal reservoirs is the possible reaction of proppants with reservoir rock and hydrothermal brines at high temperature, which could compromise their mechanical integrity, leading to increased fracturing and decreased efficacy. We reacted proppant materials of several compositions with hydrothermal brine and reservoir rock powders, then performed crush tests to assess how chemical reactions modify mechanical characteristics of the proppants. One set of samples was reacted for 7 days at 250°C and 15.9 MPa and another for 63 days at 200°C and 13.8 MPa. We find that reactions between proppant materials, brines and reservoir rock lead to minor etching of proppant surfaces and precipitation of secondary minerals, but proppants maintain mechanical integrity. The results of this study indicate that a wide range of proppant materials may be suitable for use in geothermal applications without the risk of mechanical degradation due to hydrothermal alteration.

1. Introduction

Near-wellbore conductivity is a primary factor controlling a well's economic viability. For reservoirs that lack sufficient natural permeability, reservoir stimulation treatments can be performed with the goal of improving the near-wellbore conductivity and flow capacity of a well through a variety of mechanisms. Widely adopted for use in the oil and gas industry, proppants have proven effective at maintaining conductivity for newly initiated tensile fractures following the stimulation phase and during production, even as fracture closure occurs. Initial tests of the effectiveness of proppants in geothermal reservoirs produced mixed results (Entingh, 2000); however, the widespread success of proppants in unconventional hydrocarbon reservoirs over the

last several decades has led to the suggestion that current proppant technology could be adopted for use in geothermal settings, particularly where stimulation treatment designs targeting tensile fracturing are used (Shiozawa and McClure, 2014; Norbeck et al., 2018).
The evolution of geothermal reservoir behavior is subject to thermal, hydrologic, mechanical and chemical processes. Proppants in a geothermal reservoir will be subject to the same. Some important questions that need to be answered in order to reliably predict the performance of proppants in a geothermal reservoir include: Are the proppants strong enough to withstand reservoir stresses without losing integrity? How will reactions between the proppants, lrock and formation/injection fluid affect the mechanical properties of the proppants and the fractures themselves? Will chemical reactions induce precipitation that can compromise the conductivity of fractures? To begin to address some of these questions, we adopt an experimental approach. We react several common proppant materials with well cuttings and hydrothermal brine at reservoir temperature and pressure, then examine the textural and mechanical properties of the proppants before and after reaction.

2. Materials

2.1 Proppants

Several types of proppants were tested:
(1) White Sand: clean quartz sand, 100 mesh, 30/50 mesh, 40/70 mesh
(2) Synthetic: very small spherical synthetic proppants, industrial biproduct of paint manufacture
(3) Uncured, resin-coated: uncured, resin-coated quartz sand
(4) Cured, resin-coated: cured, resin-coated quartz sand
(5) Premium, resin-coated: premium, cured, resin-coated quartz sand
(6) Brown Sand: unsorted mix of quartz and feldspar sand

2.2 Reservoir Rock

For the 7-day tests, cuttings from an experimental geothermal well were used.

Table 1: XRD results for well cuttings

Mineral	Vol%
Plagioclase	47.7
Chlorite	18.4
Biotite	13.1
Hornblende	11.8
Quartz	9.0

For the 63-day tests, two types of rocks were ground and sieved to be used for reaction with brines and proppant materials. Rock samples were taken from cores from a well at an operational geothermal power plant. The phyllite core was from 3675 to 3684 feet depth and the diorite core was from 4428 to 4438 feet depth.

(1) Phyllite: Phyllosilicate-rich, metapelitic rock.

Table 2: XRD results for phyllite sample.

Mineral	**Vol%**
Quartz	54.4
Plagioclase	30.4
Chlorite	12.2
Biotite	3.1

(2) Diorite: Intrusive igneous rock.

Table 3: XRD results for diorite sample.

Mineral	Vol%
Plagioclase	62.5
Horneblende	26.6
Graphite	6.4
Quartz	3.2
Zirconia	1.2
Chlorite	0.1

2.3 Hydrothermal Brine

Fluid from an experimental geothermal well was used to approximate the composition of realistic formation fluids.

Table 4: Composition of hydrothermal brine.

Component	Amount
Na (ppm)	2350
K (ppm)	610
Ca (ppm)	37
Li (ppm)	20
Mg (ppm)	0.5
B (ppm)	296
SiO_2 (ppm)	575
Cl (ppm)	4360
F (ppm)	6.5
SO_4 (ppm)	82
HCO_3 (ppm)	140
pH	7.71
TDS (ppm)	8470

3. Methods

3.1 Chemical Treatment

For the 7-day study, proppants were reacted with brine with and without cuttings. White sand 100 mesh, white sand 30/50, uncured, resin-coated, cured, resin-coated, premium, resin-coated and synthetic proppant were tested. Samples without cuttings contained 8g of proppant and 8 mL of brine. Samples with cuttings contained 4g of proppant, 4g of cuttings and 8 mL of brine.

All samples were loaded into Teflon vials and placed into a Parr high pressure reactor. The vessel was closed and purged of air using argon gas. The gas pressure inside the vessel was then raised to 15.9 MPa. Once pressure equilibrium was reached, the temperature was raised to 250°C. Thermal equilibrium was reached within 24 hours. The samples were then allowed to react at pressure and temperature for 7 days. At the end of the 7th day, temperature was gradually reduced to room temperature (23°C). Cooling took approximately 36 hours. Once room temperature was reached, pressure was reduced to ambient conditions, the samples removed and mechanical testing and characterization was completed.

For the 63-day study, all proppants were reacted with both brine and cuttings. White sand 100 mesh, white sand 30/50, white sand 40/70, brown sand and cured, resin-coated proppants were used. Each sample was loaded with 4g of proppant, 4g of crushed and sieved phyllite or diorite and 8 mL of brine. All samples were loaded into Teflon vials and placed into a Parr high pressure reactor. The vessel was closed and purged of air using argon gas. The gas pressure inside the vessel was then raised to 13.8 MPa. Once pressure equilibrium was reached, the temperature was raised to 200°C. Thermal equilibrium was reached within 24 hours. The samples were then allowed to react at pressure and temperature for 63 days. At the end of the 63rd day, temperature was gradually reduced to room temperature (23°C). Cooling took approximately 36 hours. Once room temperature was reached, pressure was reduced to ambient conditions, the samples removed, oven-dried and mechanical testing and characterization was completed.

3.2 Mechanical Testing

Mechanical testing was performed on each type of proppant before and after reaction. Modified crush tests were used to characterize brittleness of proppant materials. A crush tester was fabricated out of hardened steel, consisting of a cylindrical sample chamber and piston. Before tests, all samples were sieved between 30- and 50-mesh. 2g of sample was then loaded into the sample chamber of the crush tester and the piston fitted on top of the powder. The crush tester was then loaded into a hydraulic press. Axial stress was raised at a rate of 0.7 MPa/minute until a total axial stress of 27.6 MPa was achieved. This stress was held for 2 minutes, then axial stress was reduced at a rate of 0.7 MPa/minute to 0 MPa. Samples were then sieved again with a 50-mesh sieve, and the weight % of crushed material recorded. All proppants were tested 3 times before reaction. Due the small amount of reacted material, post-reaction samples were tested only once.

3.3 Characterization

All samples were characterized using SEM. Small portions of samples were affixed to SEM mounts with carbon tape and sputter coated with a thin layer of gold to prevent charging during imaging. Images were captured to characterize surface texture and presence or absence of secondary minerals. When appropriate, EDS was employed to characterize mineralogy of grains and secondary minerals.

4. Results

4.1 Crush Tests - 7-day reaction

Crush tests for the week-long reacted samples show little effect on the brittleness of all proppants, with the exception of the uncured, resin-coated sample. Little, if any reaction was observed in the samples reacted without cuttings, so crush tests were only performed on samples reacted with cuttings.

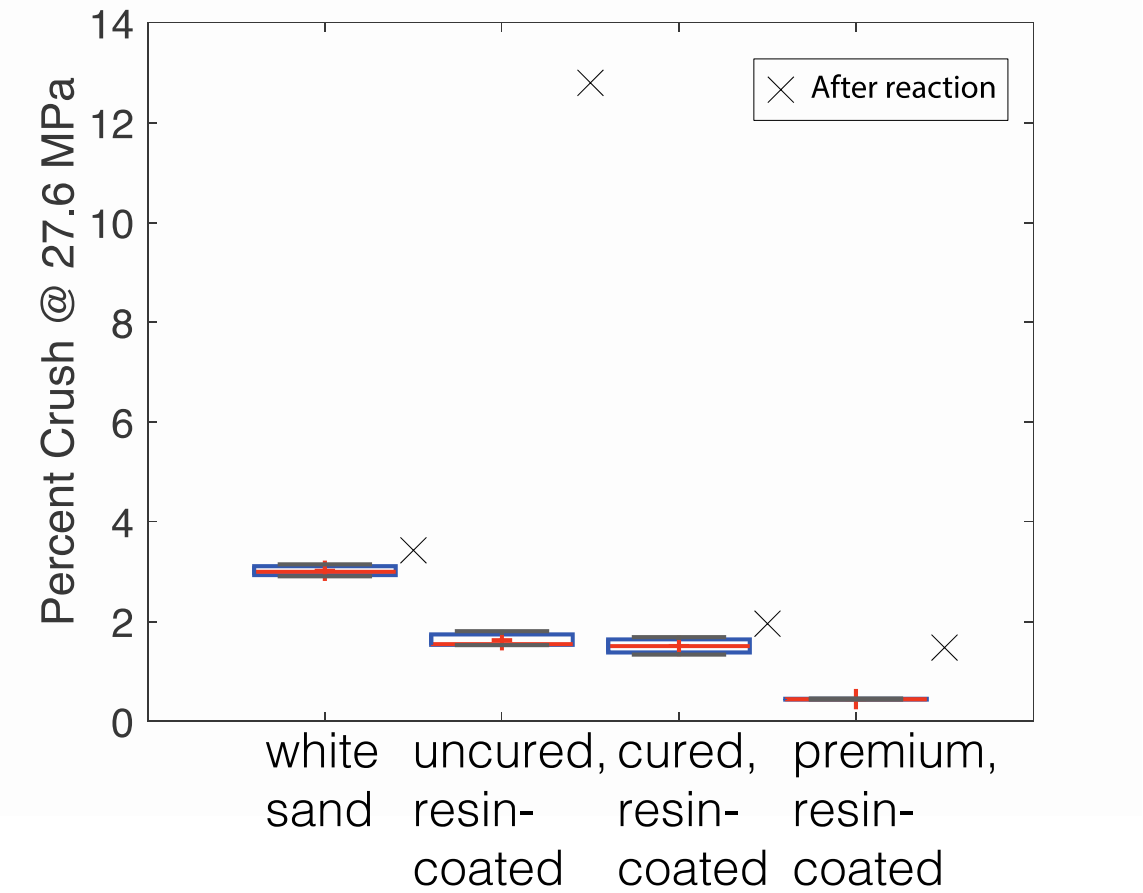

Figure 1: Results from crush tests for 7-day reactions. Red bars indicate mean values from 3 crush tests performed on pre-reaction proppants. Blue boxes represent one standard deviation and black bar represent the full extent of the data. Xs represent post-reaction data.

Pre-reaction white sand had 2.9% average crushed grains, and after this increased only nominally to 3.4%. Pre-reaction uncured, resin-coated proppant had 1.5% crushed grains, increasing substantially to 12.8% after reaction. Pre-reaction cured, resin-coated proppant had 1.5% crushed grains, increasing only nominally to 2% after reaction. Finally, pre-reaction premium, resin-coated had 0.5% average crushed grains, increasing nominally to 1.4% after reaction. Synthetic proppant grains were too small to conduct a meaningful crush test.

4.2 Imaging – 7-day reaction

4.2.1 White Sand

Little textural change on the surface of white sand grains of all size fractions. For simplicity, only 30/50 mesh size fractions are discussed. The main feature that can be seen for white sand is surface etching of the quartz sand. It is apparent that reaction with brine leads to some additional pitting, but changes are not dramatic.

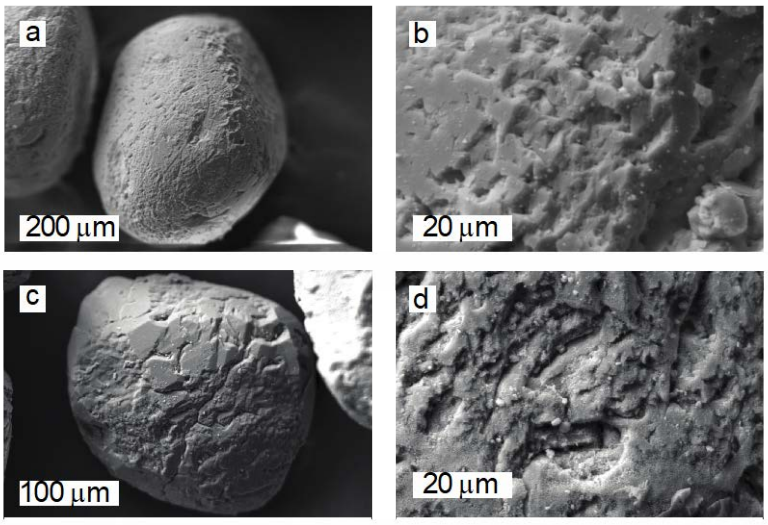

Figure 2: SEM images of white sand. a,b) Prior to reaction. c,d) After reaction.

4.2.2 Uncured, Resin-Coated

The main change in the surface texture of uncured, resin-coated proppant is due to degassing of solvent from the resin coating. This is an uncured proppant, so significant degassing is apparent. Unreacted proppants have smooth, continuous resin coatings. After reaction, the resin coating shows significant pock marks where solvent has degassed. In some areas, fresh quartz is exposed under resin.

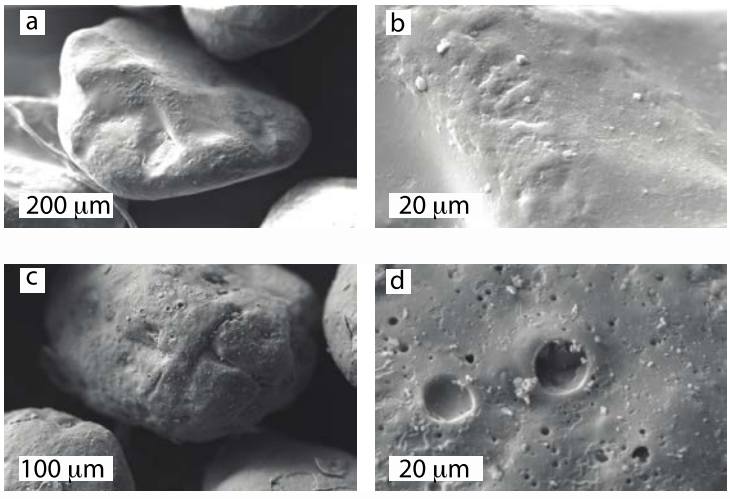

Figure 3: SEM images of uncured, resin-coated proppant. a,b) Prior to reaction. c,d) After reaction.

4.2.3 Cured, Resin-Coated

The main change in the surface texture of cured, resin-coated proppant is also due to degassing of solvent from the resin coating. Unreacted proppants have smooth, continuous resin coatings. After reaction, the resin coating shows some pock marks where solvent has degassed, though the alteration was less than observed for uncured, resin-coated proppants. Fresh quartz was not observed to be exposed in this sample.

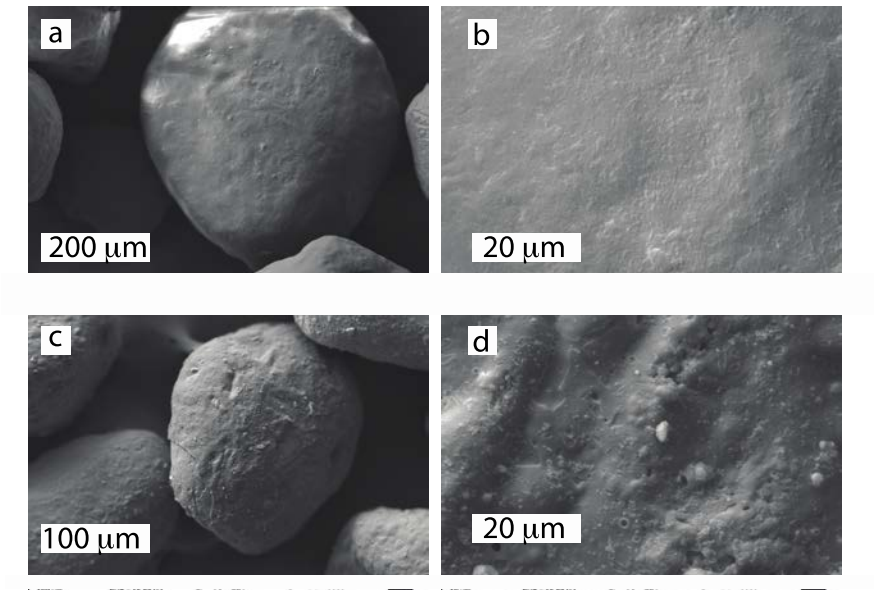

Figure 4: SEM images of cured, resin-coated proppant. a,b) Prior to reaction. c,d) After reaction.

4.2.4 Premium, Resin-Coated

Little change in the surface texture of premium, resin-coated proppant is observed. Unreacted proppants have smooth, continuous resin coatings. After reaction, the resin coating appears largely unaffected. Fresh quartz was not observed to be exposed in this sample.

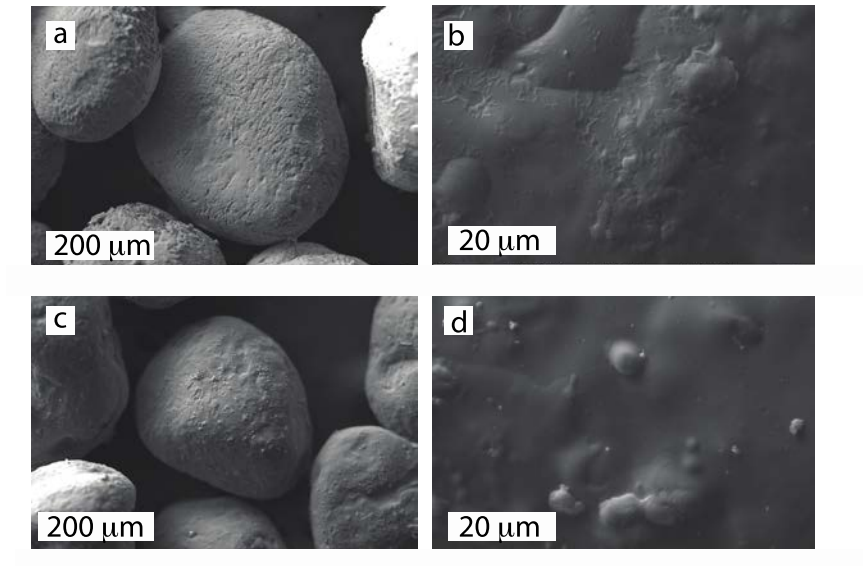

Figure 5: SEM images of premium, resin-coated proppant. a,b) Prior to reaction. c,d) After reaction.

4.2.5 Synthetic Proppant

The synthetic proppant grains were much smaller than other proppants, so were more difficult to image in detail. They appear extremely spherical, with grain sizes from 20 to <1 micron. Surfaces appear smooth. No significant change was observed after reaction.

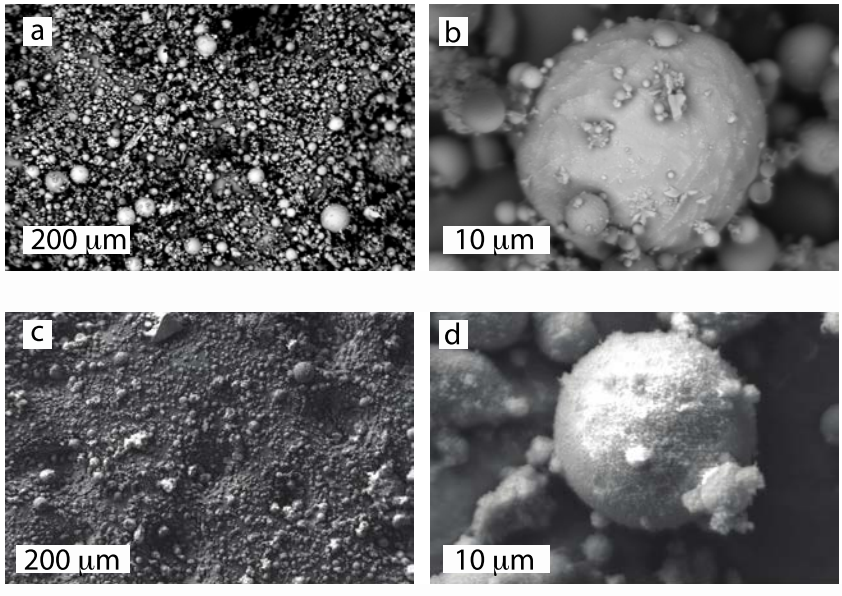

Figure 6: SEM images of synthetic proppant. a,b) Prior to reaction. c,d) After reaction.

4.3 Crush Tests - 63-day reaction

Crush tests for the 63-day reacted samples also show little effect on the brittleness of all proppants investigated. Slightly more reaction was observed in samples reacted with diorite.

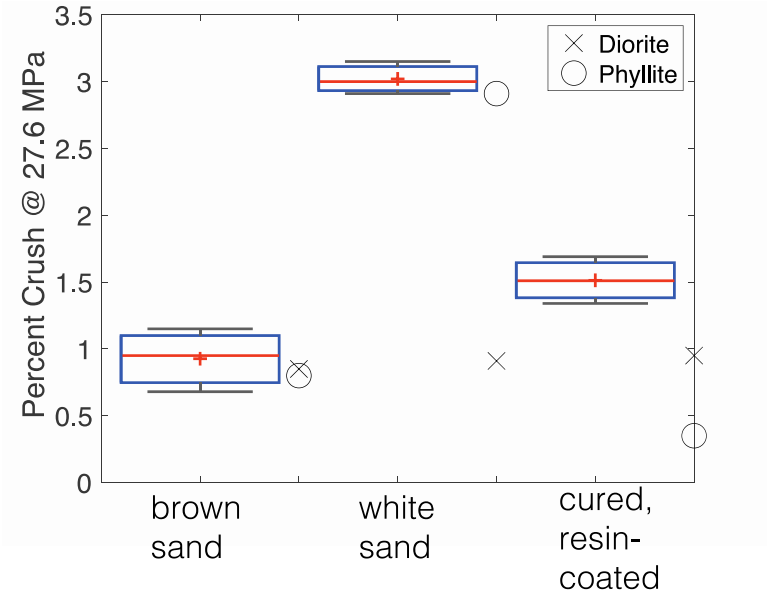

Figure 7: Results from crush tests for 63-day long reactions. Red bars indicate mean values from 3 crush tests performed on pre-reaction proppants. Blue boxes represent one standard deviation and black bar represent the full extent of the data. Xs represent samples reacted with diorite and Os represent samples reacted with phyllite.

Pre-reaction brown sand had 1% average crushed grains, and after this decreased only nominally to 0.9% for diorite and 0.8 for phyllite. Pre-reaction white sand had 2.9% average crushed grains, and after decreased to 0.9% for diorite and 2.8% for phyllite. Pre-reaction cured, resin-coated proppant had an average of 1.5% crushed grains, decreasing to 1% for diorite and 0.4% for phyllite.

4.4 Imaging – 63-day reaction

4.4.1 White Sand

The longer reaction time does not appear to have led to appreciably more pitting of the surface of white sand grains. The sample reacted with phyllite appears very similar to unreacted and 7-day reacted samples. The sample reacted with diorite appears to have similar levels of pitting but also shows limited precipitation of fine-grained, platy minerals on the surface of grains.

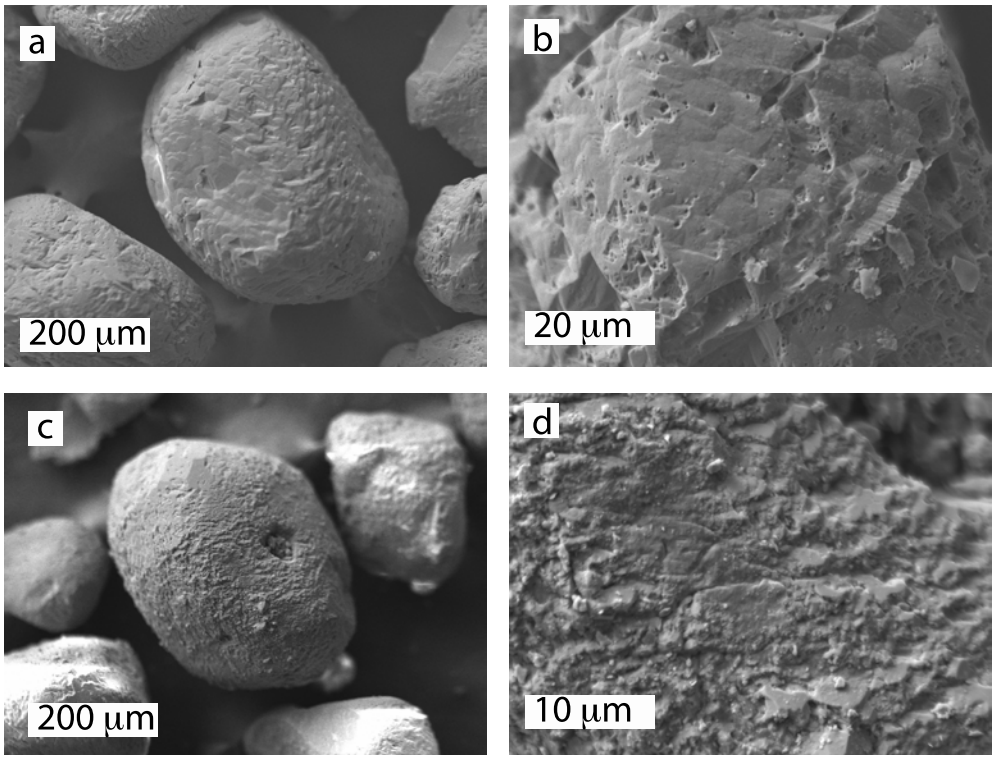

Figure 8: SEM images of white sand. a,b) Proppant reacted with phyllite powder. c,d) Proppant reacted with diorite powder.

4.4.2 Brown Sand

The brown sand samples show the largest degree of alteration of all the samples considered. Unaltered samples have clean, smooth surfaces. Samples reacted with phyllite show little evidence of dissolution, but do have some precipitation of secondary minerals on grain surfaces. Samples reacted with diorite also show little evidence of dissolution, but have significant precipitation of secondary minerals on grain surfaces. Secondary minerals are all fine-grained with platy habits, which we interpret to be clay minerals created by reaction of feldspar minerals with brine.

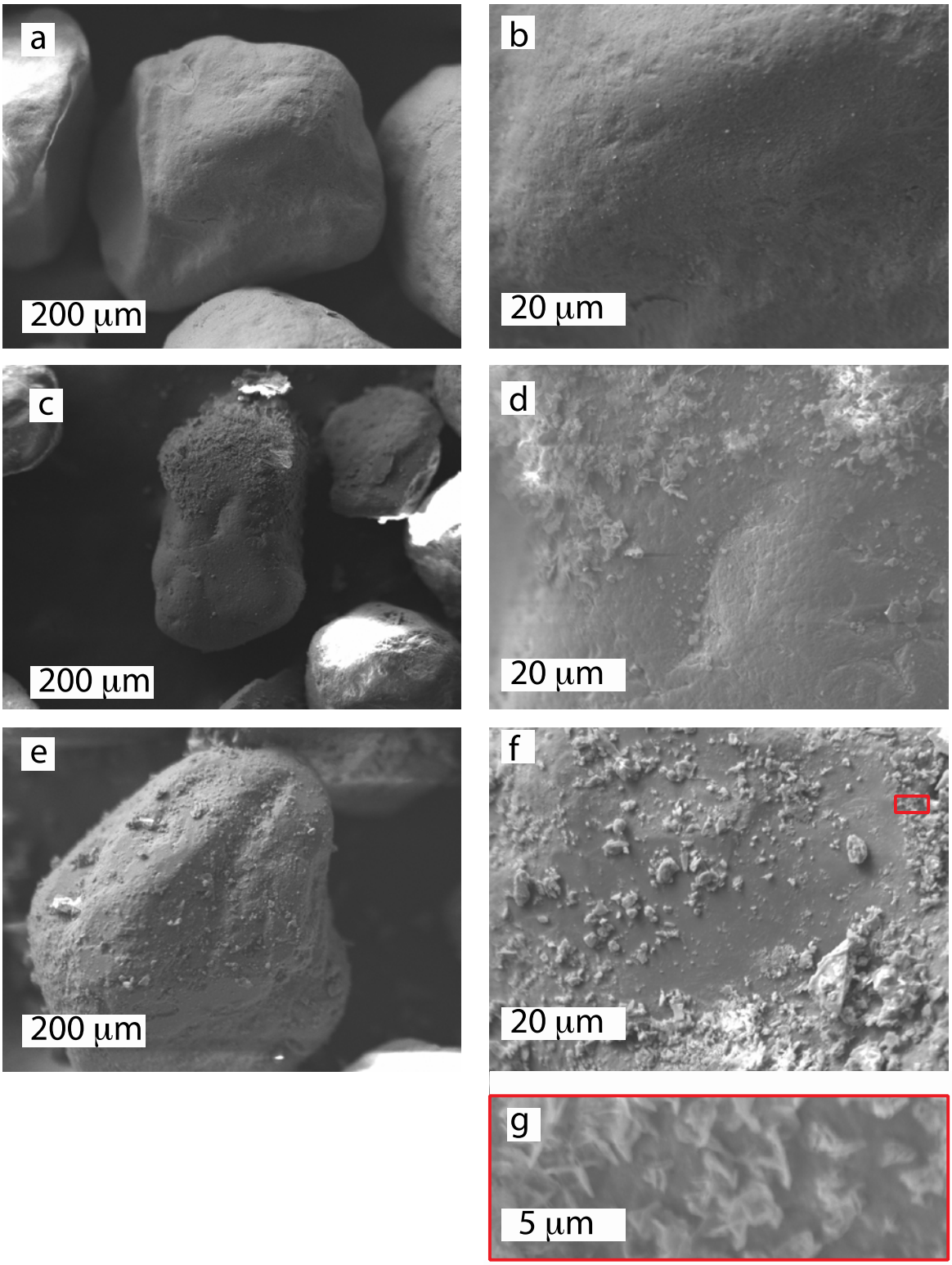

Figure 9: SEM images of brown sand. a,b) Prior to reaction. c,d) Proppant reacted with phyllite powder. e,f) Proppant reacted with diorite powder. g) Close-up of platy secondary minerals.

4.4.3 Cured, Resin-Coated

The cured, resin-coated proppant does not appear to be significantly affected by the 63-day reaction. The sample reacted with phyllite shows small pocks as a result of degassing of solvent from resin and some deposition of secondary minerals on grain surfaces. The sample reacted with diorite looks similar to the sample reacted with phyllite with slightly more secondary minerals.

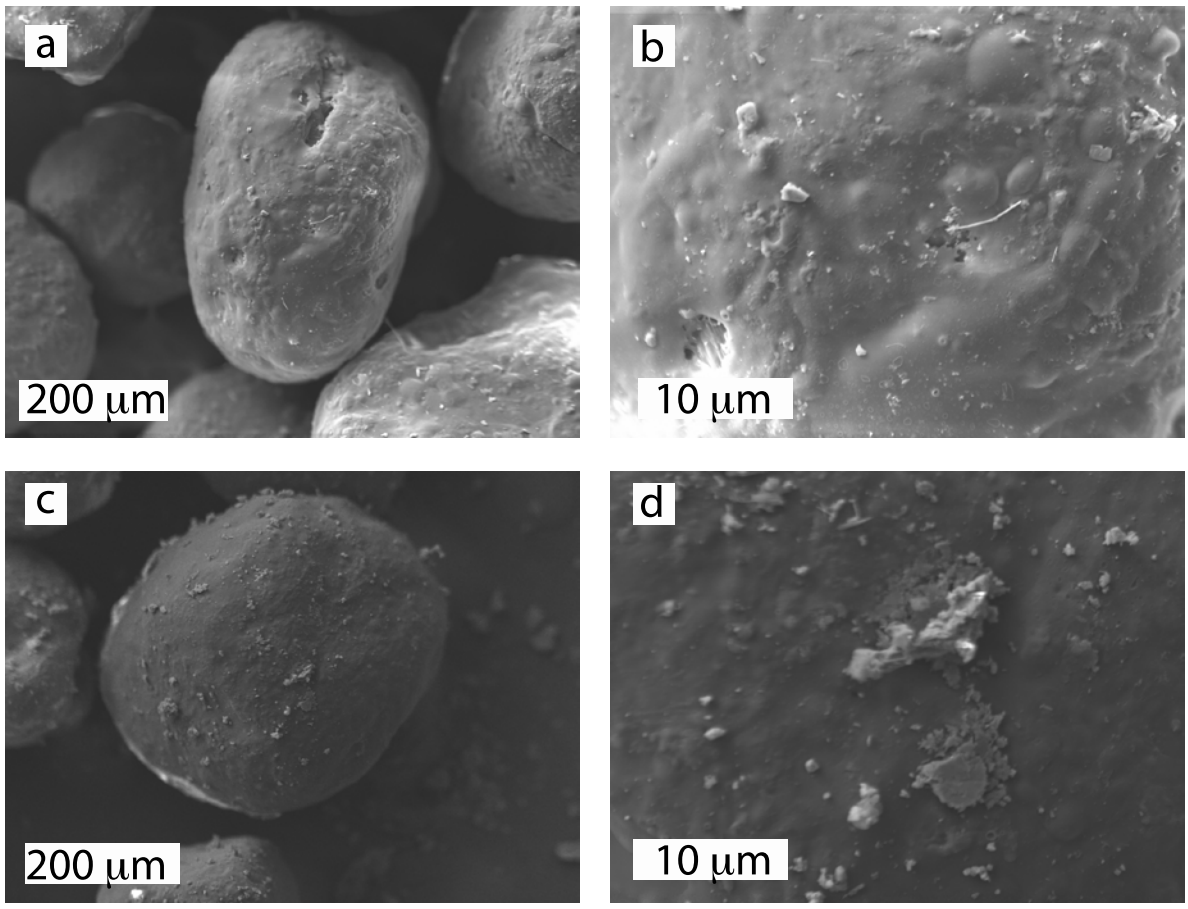

Figure 10: SEM images of cured, resin-coated proppant. a,b) Proppant reacted with phyllite powder. c,d) Proppant reacted with diorite powder.

5. Discussion

Our experimental result is in fairly good agreement with the literature. We find that, with the exception of feldspar-rich brown sand, only minor dissolution or secondary precipitation is caused by reaction of proppants with brine and reservoir rock at 14-16 MPa and 200-250°C. Mclin et al. (2010) and Brinton et al. (2011) studied bauxite and quartz proppants in typical geothermal brines at 230°C and, in agreement with our results at similar conditions, observed little chemical alteration. Lee et al. (2010) examine bauxite and quartz proppants at 121-191°C and ambient pressure to 65 MPa and find pressure solution processes can result in permeability reductions up to 75% in 1000 days. Deon et al. (2013) studied bauxite proppants in high salinity brines from ambient temperature to 150°C and found that saline fluids induce higher rates of

dissolution and the precipitation of salts and zeolites. Jones et al. (2014) study quartz and bauxite mixed with crushed quartz monzonite and brine at 225-275°C and observe little reaction at lower temperatures and the production of opal and zeolites at higher temperatures, although the secondary minerals were likely the result of dissolution of glass ampules used to contain the reactions.

Relatively less attention has been paid to the mechanical performance of proppant materials after hydrothermal reaction. Mattson et al. (2016) studied quartz, bauxite and another ceramic proppant using a similar methodology to this study at 250°C and found limited chemical alteration caused minor mechanical weakening of bauxite and more significant weakening for the ceramic proppant, but were unable to quantify the effect on quartz. It is difficult to directly compare the results of this study with those presented here due to differences in proppant composition, but in general the findings that hydrothermal reaction leads to only modest mechanical effects within several months is consistent with our result.

One interesting finding of this study is that less well-sorted sands that include higher fractions of feldspar, which tend to be less expensive, produce more secondary mineralization under hydrothermal conditions. This dissolution-precipitation reaction does not appear to cause significant alteration of proppant mechanical characteristics; however, more study of whether the production of fine-grained secondary minerals can cause significant reductions in permeability is warranted.

6. Conclusions

The major finding of this study is that reactions between common proppant materials, hydrothermal brine and reservoir rock do not have significant effects on the mechanical behavior of proppants at 13-16 MPa and 200-250°C. Quartz-dominated proppants and resin coated proppants are particularly unreactive. Formation fluids hosted in silica-rich igneous or metamorphic rocks are likely saturated in quartz, so dissolution of quartz is not substantial. Cured resin adds an additional barrier to dissolution of quartz, but may be unnecessary in many cases. Proppants that contain substantial amounts of feldspar minerals are likely to be more reactive, resulting in dissolution of feldspar and precipitation of clays. The data from this study do not suggest that clay precipitation has a substantial role on the overall brittleness of the proppants. The presence of secondary minerals on white sand and resin-coated grains in 63-day tests suggests that some production of clays is due to reaction of the crushed reservoir rock with brine. In-situ, reservoir rock and brine may be closer to equilibrium, leading to less production of clays.

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