

Recovery of Reservoir Permeability by Acid Injection in the Margretheholm-1 Geothermal Well - Potential Risk Assessment

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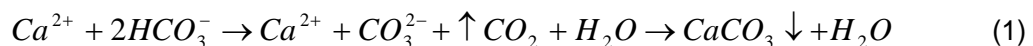
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1. Introduction and Background.

The Margretheholm geothermal plant located approximately 5 km from the city center of Copenhagen was put in operation in 2004. Warm (75 °C) saline water (TDS 215 g/L) is being pumped from the Bunter Sandstone reservoir (2700 m) at a rate of 130 to 220 cubic meters per hour. In order to maintain reservoir pressure and to avoid environmental problems due to the high salinity water is re-injected after cooling.

Occasionally pressure increase has been observed in the Margretheholm-1 injection well, indicating clogging due to either precipitation or presence of suspended matter in the water after cooling. The problems were solved by injecting acid into the well for shorter periods of time, however, concern have risen whether the sandstone constituting the reservoir may disintegrate due to dissolution of cementation. If this should happen, the injection well may be permanently damaged. It was also stated that problems with pressure build-up mainly occurs when one does not succeed in keeping the temperature of the injected water below 20 °C. An outline of the injection problem and its likely cause was forwarded in a mail (October 14th 2010) to GEUS from J. Magtengaard, DONG Energy, asking GEUS to come up with suggestions to asses the potential risk of permanent reservoir damage. An English translation of the mail can be found in Appendix A.

Problems due to precipitation of calcium carbonate in the Margretheholm geothermal plant was not predicted before the plant was put in operation. Considering the Bunter formation water chemistry calcium carbonate should be more soluble in the water after cooling, based on general chemical knowledge assuming no degassing of carbon dioxide /1/. J. Magtengaard in a personal call informed us that degassing of formation water was necessary prior to cooling to maintain pressure below the maximum allowed for the heat exchangers. During degassing some carbon dioxide most likely is lost which will affect the solubility of calcium carbonate according to the equation below:



The necessity of degassing of formation water during operation had not been foreseen in the assessment on potential scaling problems /1/, since bubble point was calculated to be fairly moderate ca. 12 bars based on measurements of the dissolved gas content in pressurized bottom hole samples /2/. According To J. Magtengaard the bubble point was around 22 bars in practice, too high a pressure for the heat exchangers to withstand.

Maintaining the injection temperature below 20 °C in order to avoid carbonate precipitation was not always possible since the geothermal production had to adjust to the Amager power plant operation. Therefore, geothermal production totally avoiding carbonate precipitation was not a realistic option. With this in mind GEUS commented on the information provided by DONG Energy and sat up a proposal including study of acid treatment on 1) cuttings and 2) side-wall cores,. The proposal was mailed to DONG Energy November 11th 2010. An English translation of the mail can be found in Appendix B.

By mail of November 15th 2010 DONG Energy accepted the proposal without further comment.

Later, however, it turned out that no side-wall cores had been taken in Bunter Sandstone Formation in neither of the two wells of the Margretheholm doublet. Side-wall cores had been taken only in the shallower Gassum Formation. This meant that only the second option proposed by GEUS (Appendix B), existed in reality. After a quick inspection of cutting samples available it was realized that the samples offered very limited possibility to study the cementation pattern of the sandstone. It was therefore decided to perform acid experiment on suitable core plugs from the Bunter Sandstone Formation recovered from St19 well, at Stenlille natural gas underground storage. The Stenlille-19 (St19) well is located approximately 70 km from Copenhagen.

2. Selection of Reservoir Rock Material for Testing

Cold water is being injected into the Bunter Sandstone Formation through the casing perforations 2489 – 2662 m below surface. A flow log indicated that most part of the water entered the formation interval from 2489 to 2575 m. So, material from within this interval would be most relevant to study with respect to its stability during acid treatment. The intervals at 2510 m and 2535 were chosen as representative of the Bunter Sandstone Formation as these cuttings samples had the highest content of sandstone fragments. The interval 2686 m was taken as a reference sample as it contained kaolinised basement fragments, and was not expected to contain carbonate cement. The amount of material that could be obtained from existing washed and dried cuttings was insufficient for the acid treatment experiments. Therefore, three samples of wet cuttings, selected from the GEUS repository, were washed on a 0.36 mm sieve and dried. Furthermore, a suitable subsample (2491.17 m) was obtained from the Bunter Sandstone core from the St-19 well.

Photos of the samples intended for the acid experiments were forwarded to DONG Energy, for acceptance prior to the start of any of the experiments. A few of the photos are included in this report to illustrate the type of material available for the study of reservoir stability.

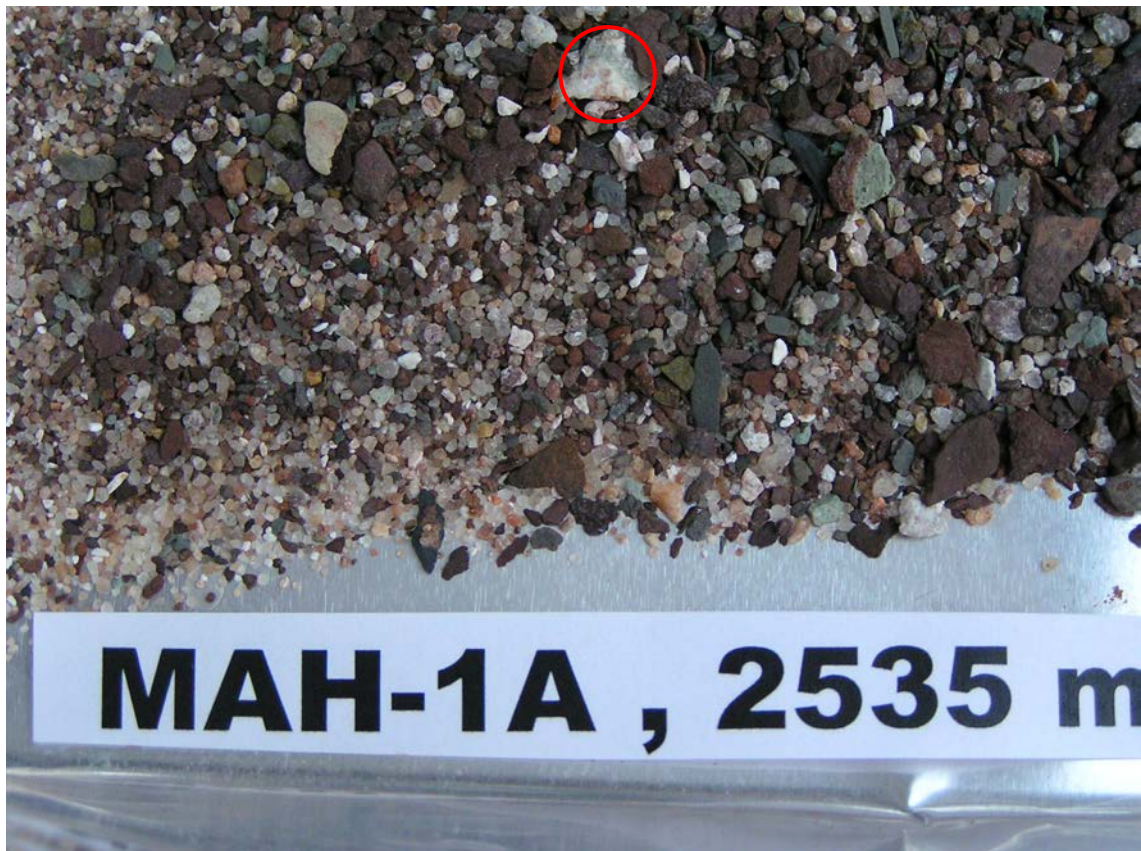


Figure 1. Close-up photo of the finer fraction of washed and dried cuttings



Figure 2. Three samples of washed and dried cuttings selected for acid experiments

Table 1. Percentage of finer and coarser cuttings

Fraction	2510 m	2535 m	2686 m
Fine; $0.36\text{mm} < x < 2.0\text{ mm}$	48	28	78
“Coarse” ; $> 2.0\text{ mm}$	52	72	22

The grain size of the cuttings varies considerably, the smaller ones being mostly individual sand grains (Figure 1), whereas the larger ones are mostly clasts of finer material, silt or clay (Figures 1-2). Very few of the sand grains appear to be cemented from the mere looks of the sample, one example may be the one indicated by the circle.

It's difficult to assert to what extent the cuttings shown in Fig. 2 represents the lithology of the 10 metre interval drilled before sampling. The mud-clasts may result from caving or may represent layers of fine-grained material in the Bunter Sandstone Formation. As the fine grained layers are of no or only little importance for the production/injection during operation of a geothermal plant, the larger clasts was discarded for the acid experiment by sieving the samples through a 2.0 mm sieve. The relative amounts of fine and fine and "coarse" cuttings were determined by weighing the samples (Table 1).

The subsample of the Bunter Sandstone Formation selected from a core of St19 well, is shown in Fig. 3.



Figure 3. Subsample of St19 core selected for acid experiment.

3. Acid Reaction Experiments on Cuttings.

The intention of acid experiment on cuttings samples was to get an idea of the stability of the sandstone when exposed to a hydrochloric acid solution with a pH around pH = 1. The experiments were performed by slow titration of suspended cuttings in de-ionized water adding 0.1 molar hydrochloric acid from a burette (Fig. 4). A magnetic stirrer was used to keep the cuttings in suspension.



Figure 4. Laboratory set-up for acid titration experiment

3.1 Titration Curves.

Approximately 8-9 grams of the fine fraction ($0.36 < x < 2.0$ mm) of cuttings was weighed and transferred to a 50 cc plastic cup, 15 mL of de-ionized water was added after which 0.1 M HCl was slowly added while reading the pH of the solution. The pH dropped from above 9 to neutral after the addition of the first millilitre of acid, Fig. 5-above.

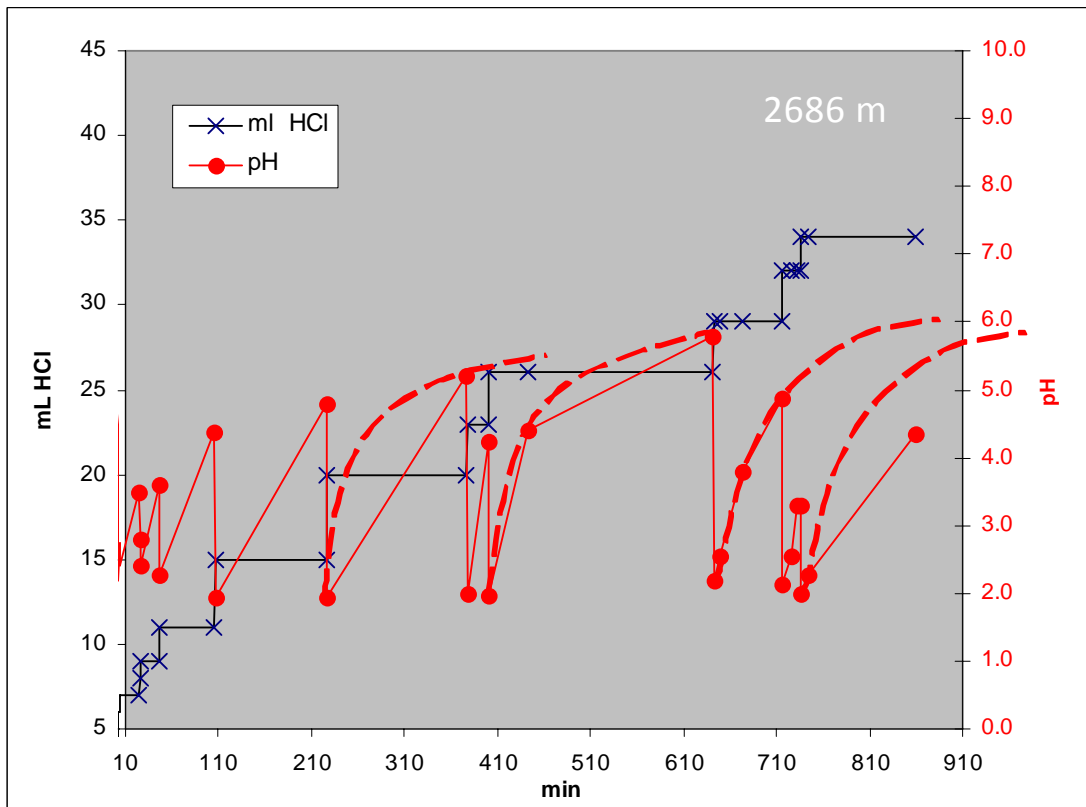
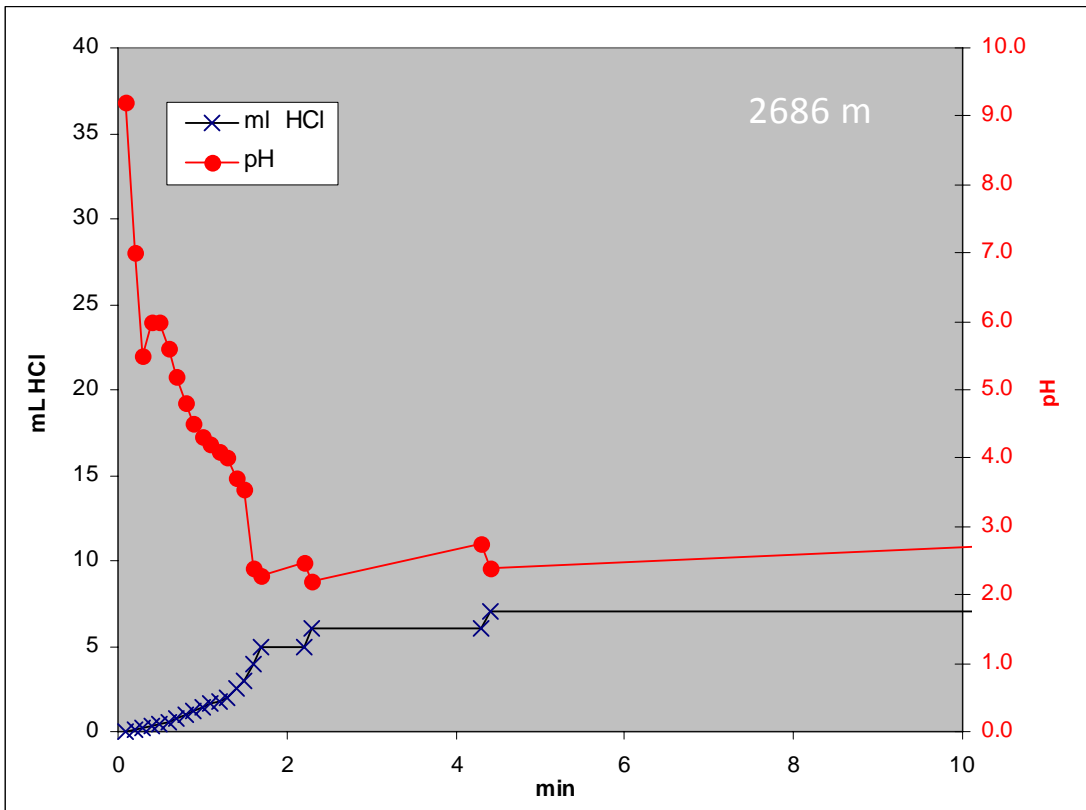


Figure 5. Change in pH with time as acid is gradually added to 8.77 gram of cuttings. Upper curves represent the small increments of acid addition at the start of the titration. Broken curves represent idealized change of pH assuming continuous monitoring.

After addition of two millilitres of acid the pH reached a value of 2.2. However, a slight increase in pH was observed after a short pause in the acid addition indicating that a reaction took place. As the solution is only weakly acidic the reaction taken place is no doubt connected with the dissolution of calcium carbonate. The significant drop in pH, while adding the first millilitre of acid (Fig. 5-upper) is most likely due to reaction with a small residue of the strongly alkaline drilling fluid.

After the pH had reached 2 the acid was no longer added continuously at a slow rate, rather certain increments were added from time to time allowing the pH to increase to almost neutral in order to follow the rate of carbonate dissolution. The pH had to be read from the display, and could not be continuously monitored with the simple instrument being used (Fig. 4). Instead idealized curves of pH change with time were drawn from the data points during time intervals of no acid addition, broken curves Fig. 5-lower. After addition of the first 32 mL of acid the pH increase with time appeared to be significantly slower than before (Fig. 5-lower). This was taken as evidence that most of the carbonate in the cuttings had been dissolved. Finally, the percentage of calcium carbonate in the cuttings was calculated, Table 2, using the expression of eq. 2.

The acid titration was repeated for the cuttings samples from both 2535 m (Fig. 6) and 2510 m (Fig. 7).

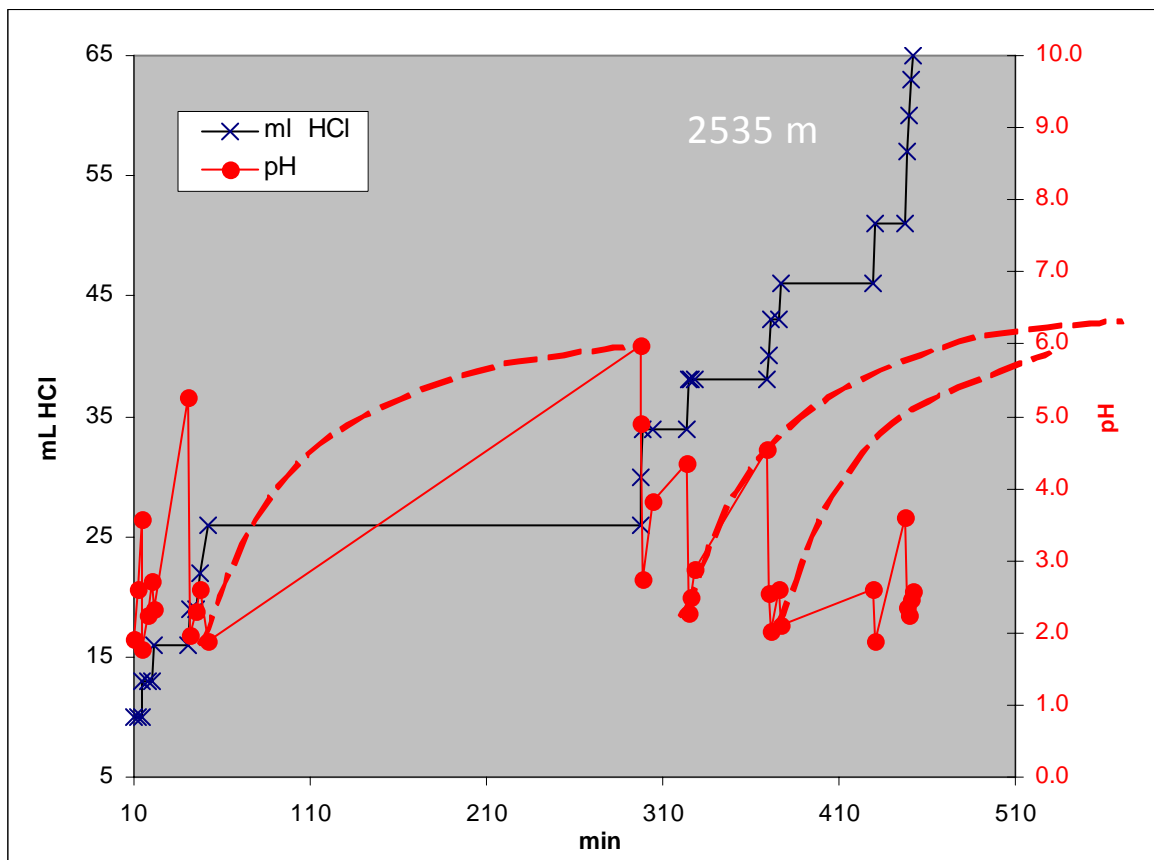


Figure 6. Change in pH with time as acid is gradually added to 9.27 gram of cuttings

The percentage of calcium carbonate in the two cuttings samples were calculated too, Table 2, showing that the percentage of carbonate in the 2535 m cuttings was about twice that of the other two cutting samples.

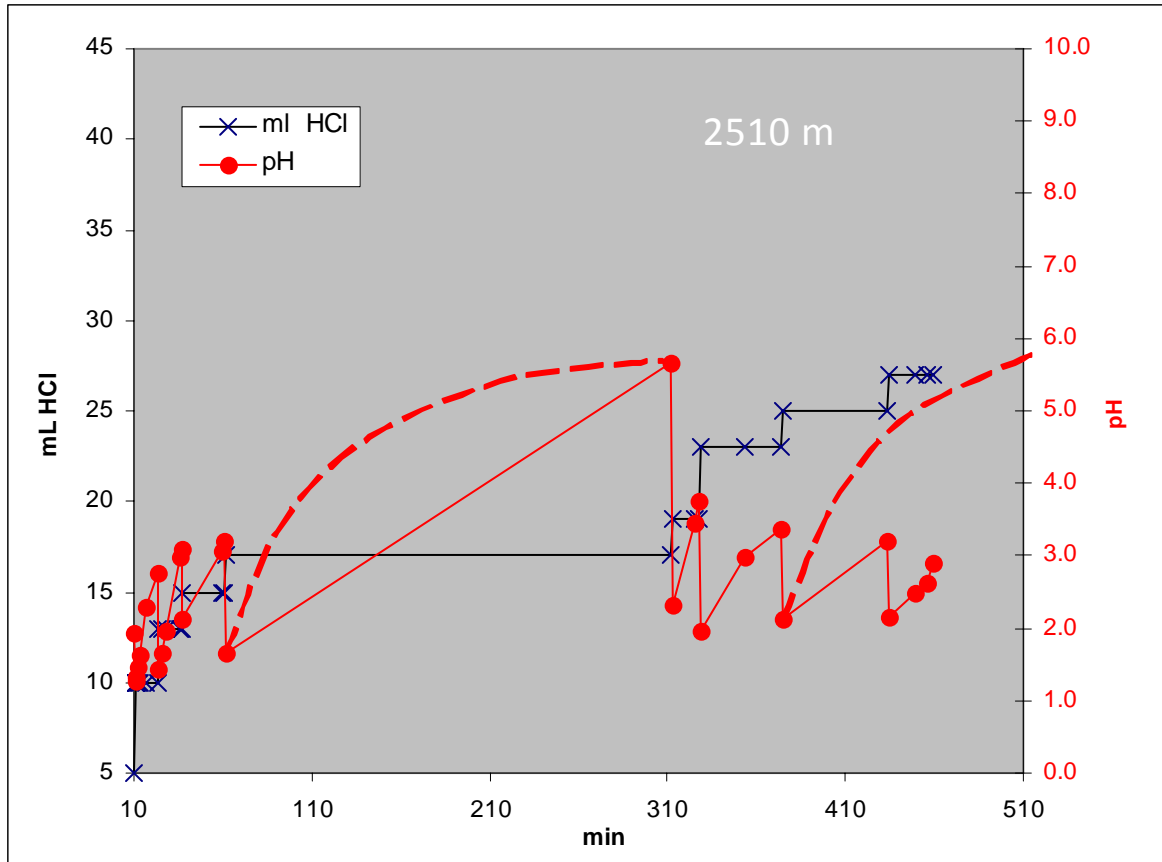


Figure 7. Change in pH with time as acid is gradually added to 7.92 gram of cuttings

$$\text{CaCO}_3 \text{ wt\%} = \text{mL(HCl)} \cdot 0.1 \cdot 0.5 \cdot \text{MWCaCO}_3 \cdot 100\% / \text{mg sample} \quad (\text{eq. 2})$$

Table 2. Calcium carbonate content (wt%) calculated

Sample	2510 m	2535 m	2686 m
Quantity g	7.92	9.27	8.77
mL 0.1 M HCl	27	65	34
CaCO ₃ wt %	1.70	3.51	1.94

3.2 Microscopy on Cuttings

In order to study the effect of acid reaction with the cuttings all three samples were filtered and dried after the completion of the acid titration. The sample appearance after the acid treatment indicated that part of the cuttings had disintegrated producing very fine grained material. Each sample was studied under a simple digital microscope (Fig. 8) allowing the full suite of grain sizes ($0.02 < x < 2.0$ mm) to be studied.



Figure 8. Digital microscope applied producing the micrographs of Figs. 9-14.

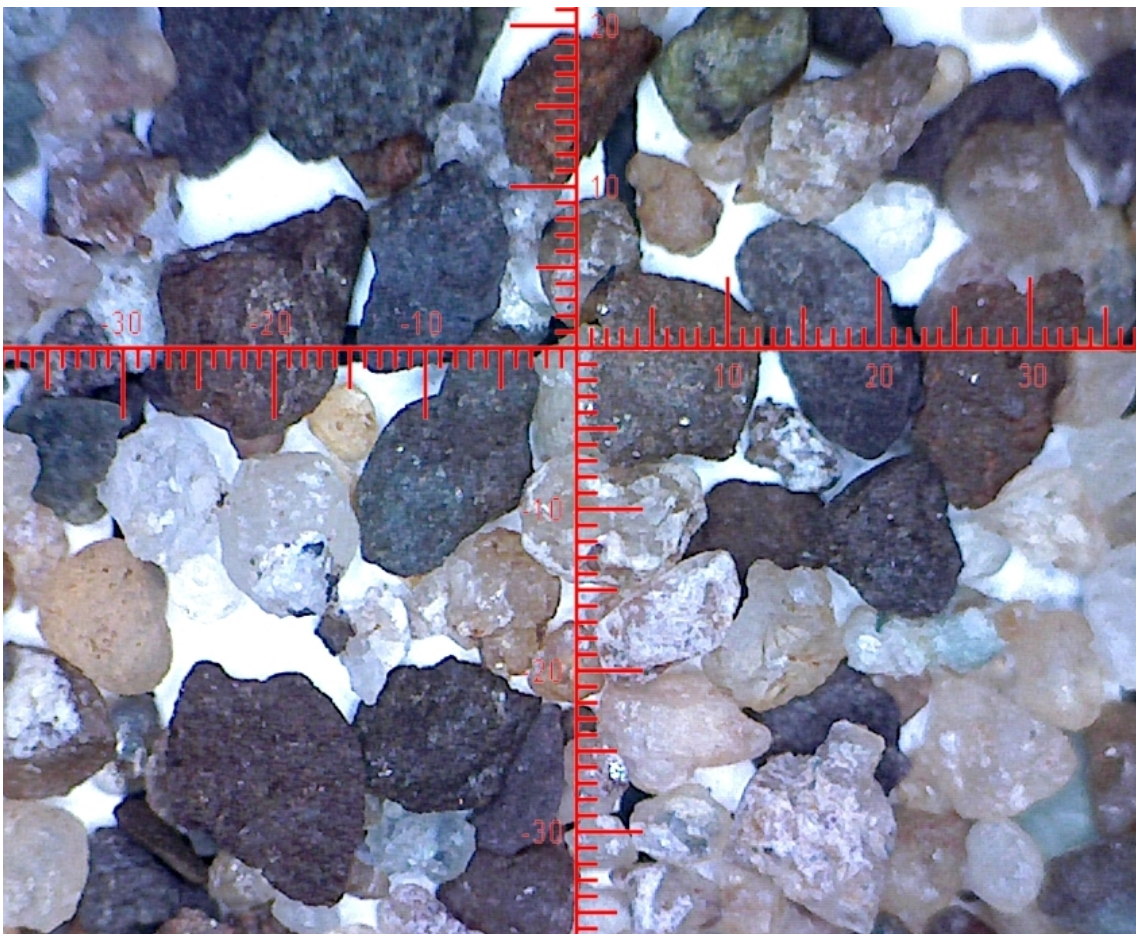


Figure 9. Micrograph (width ~7 mm) of cuttings MAH-1, 2686 m prior to acid treatment.

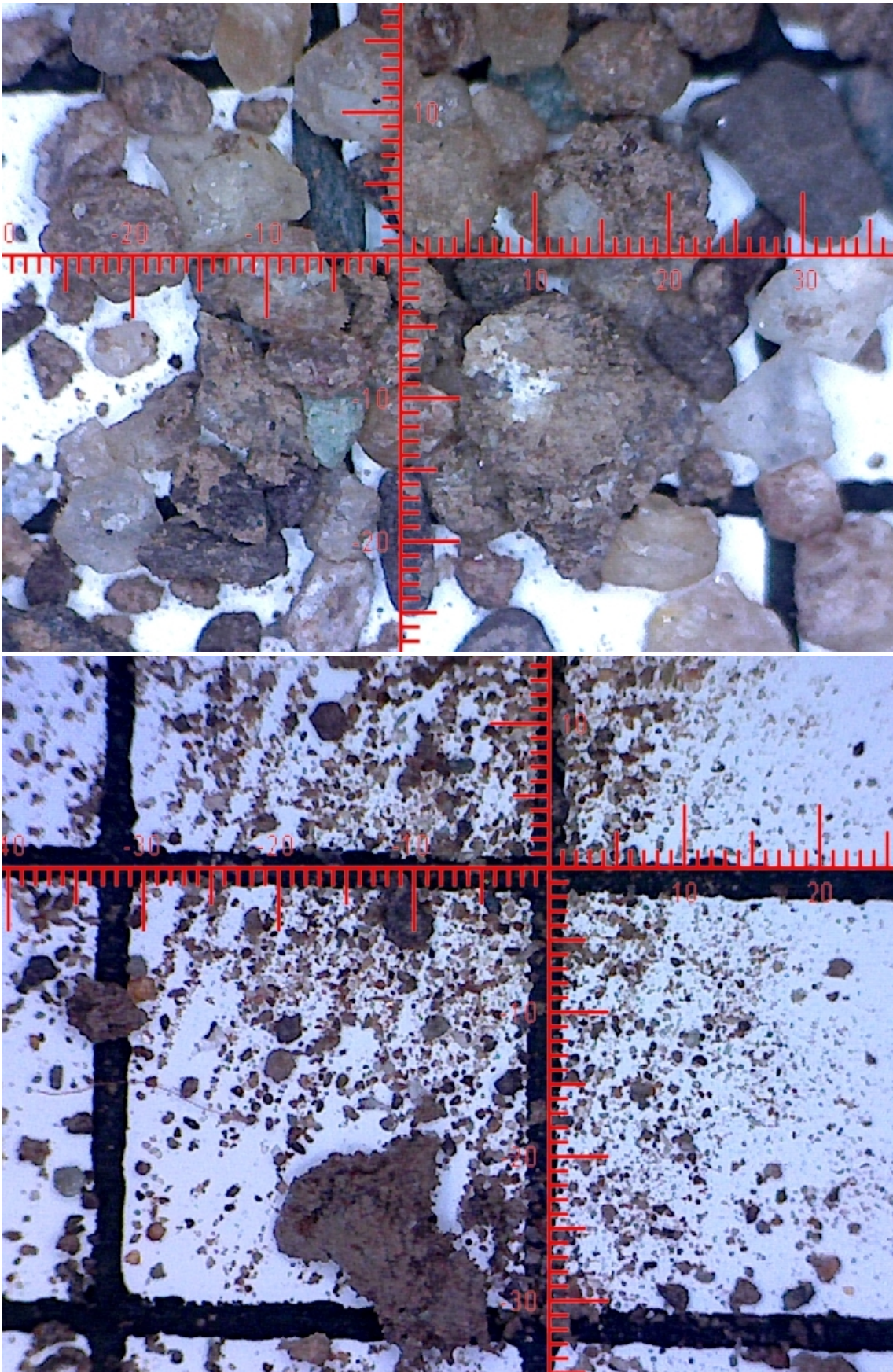


Figure 10. Micrographs of cuttings MAH-1, 2686 m after acid treatment.

The samples were studied both before and after the acid treatment. A portion of the dried cuttings was spread on a piece of filter paper marked with 3x3 mm grid lines, clearly seen on Fig 10. The distance between the object and the lens was adjusted so that the size of the area covered was about 8x10 mm, scale bar marks (in red) for each 0.1 mm is shown for particle size determination. The simple microscope could not produce a sharp picture for the whole of the 8x10 mm area, so only that part of the picture which is in focus is shown in the micrographs. Which is why the crossing of the scale bars is not located in the centre of the Figs. 9-14, as it was on the original photos.

From the simple photos of the cuttings in Figs. 1-2 one got the impression that finer cuttings consisted of mostly single grains from sandstone whereas the larger ones were clasts of silt or clay-stone. However, the micrographs reveal that the finer cuttings that passed through the 2.0 mm sieve did not represent sandstone material alone, since materials from fine grained rocks was obviously also present. Comparing the micrographs of cuttings before and after acid treatment it is concluded that most carbonate dissolved by acid was present in the cuttings of fine-grained rock material which therefore disintegrated producing fine particles, seen clearly on the lower micrograph of Fig. 10. Also, the surface of the coarser grains appears less shiny after the acid treatment than before, which is no doubt due a cover of very fine particles on their surface.

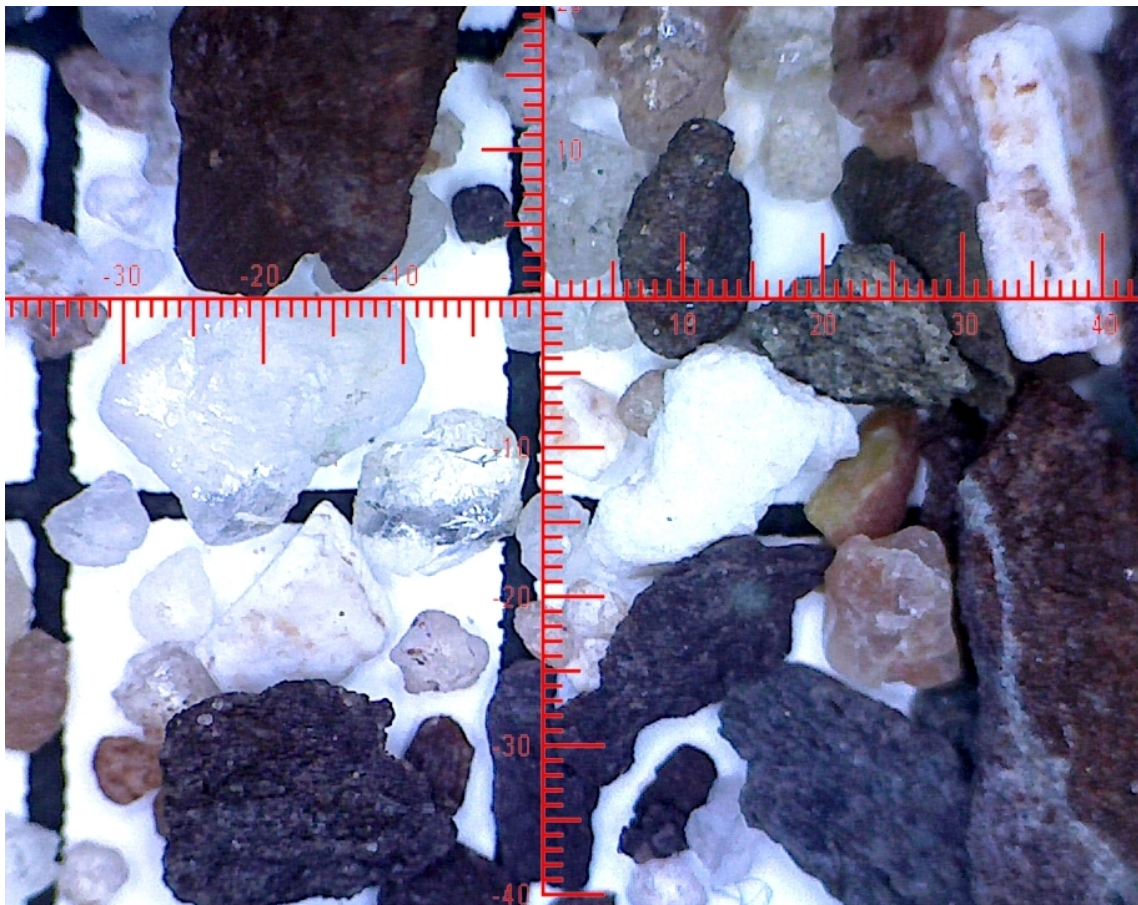


Figure 11. Micrograph (width ~8 mm) of cuttings MAH-1, 2535 m prior to acid treatment.

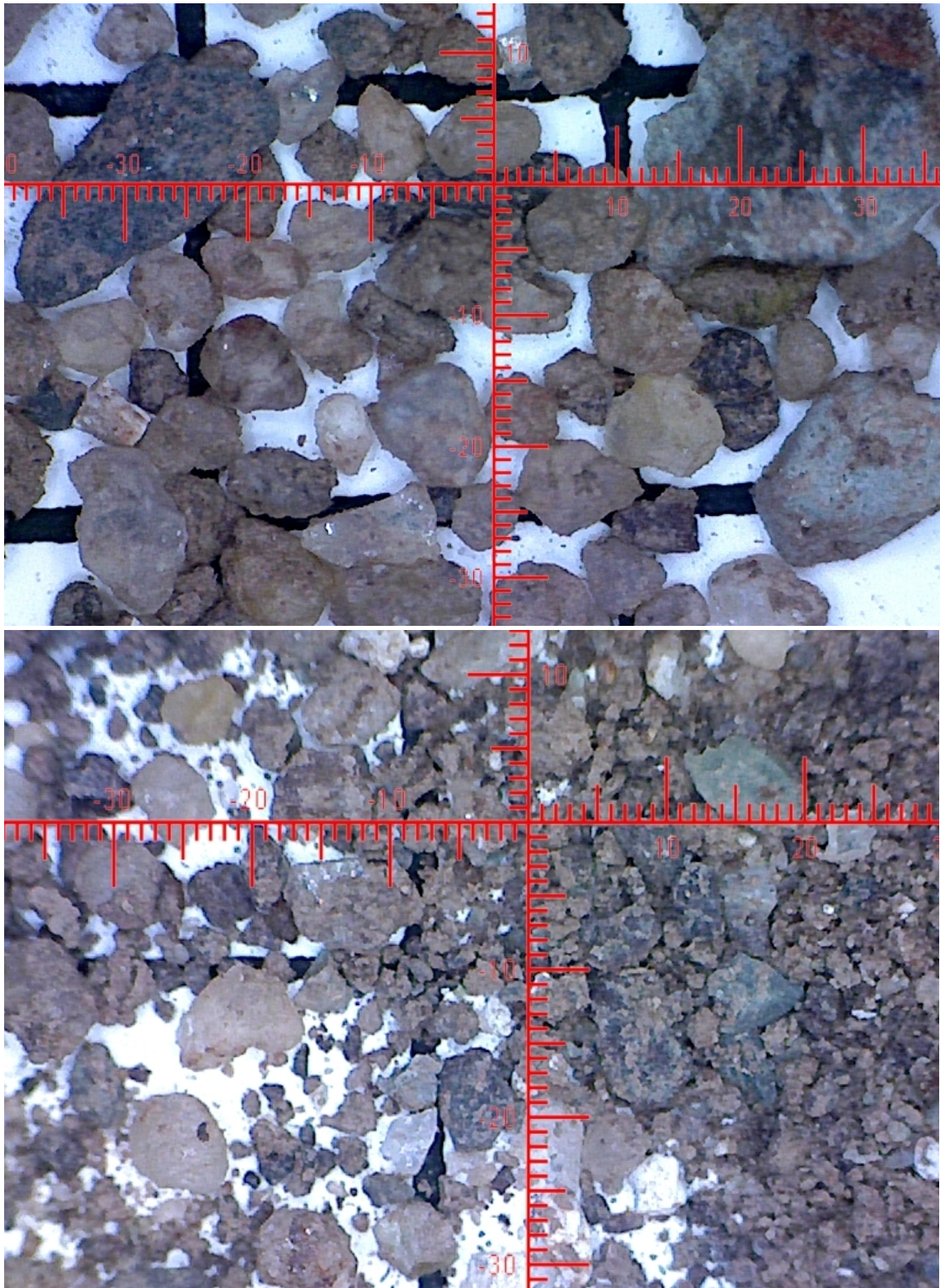


Figure 12. Micrographs of cuttings MAH-1, 2535 m after acid treatment.

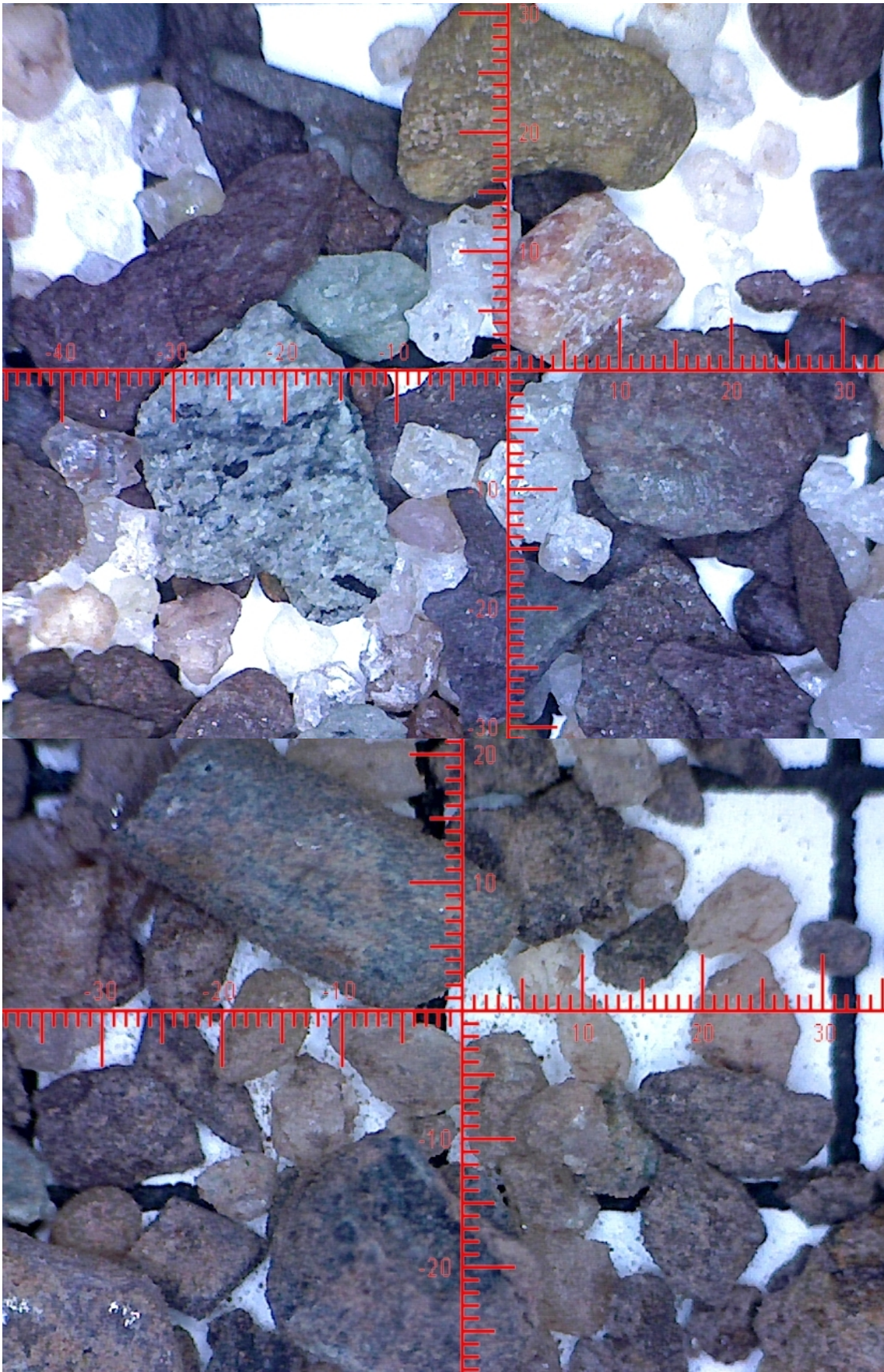


Figure 13. MAH-1 cuttings, 2510 m, before (upper) and after (lower) acid treatment.

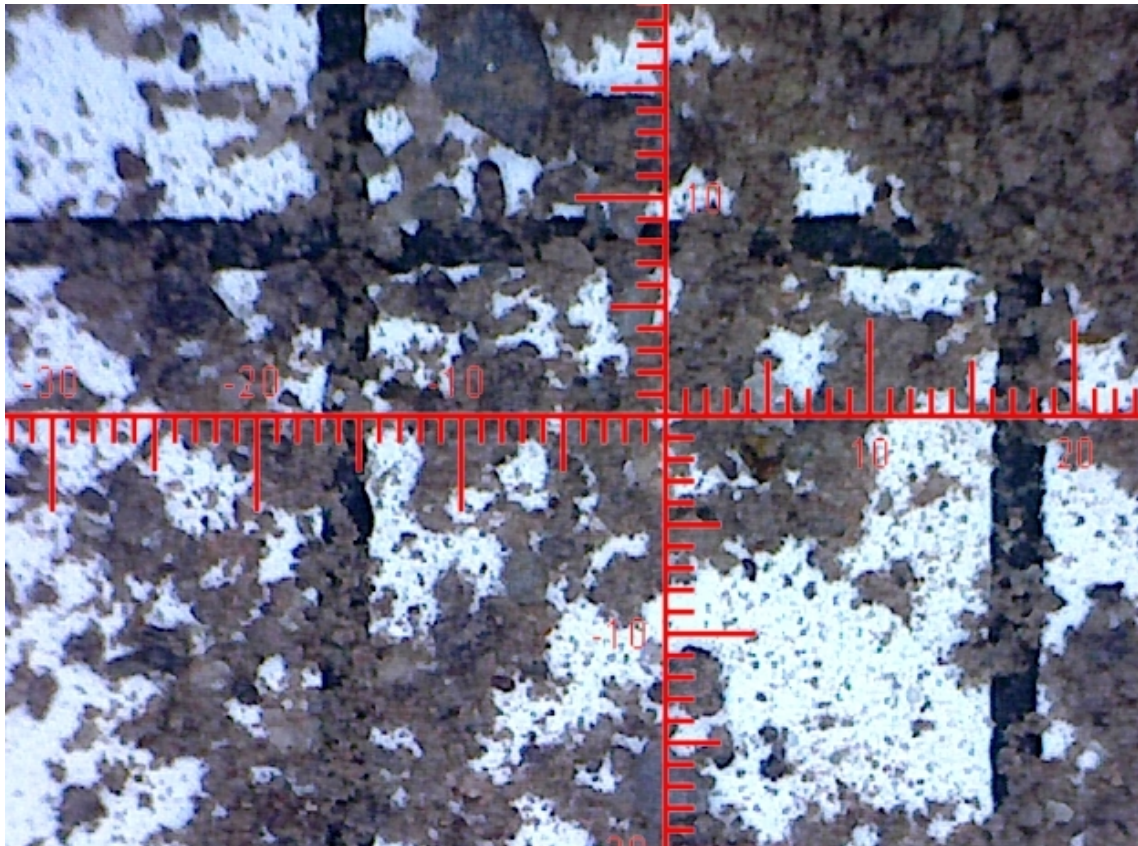


Figure 14. MAH-1, 2510 m, cuttings (fine fraction) after acid treatment.

It is very difficult if not impossible to draw any conclusion as to the kind of cementation that fix the position of the individual grains in the Bunter sandstone by just looking at the cuttings shown in Figs. 9-14. Acid titration of sieved cuttings ($0.36 < x < 2.0$ mm fraction) combined with the simple microscopic investigation show that carbonate is present, but most of it appear to exist in the fine grained layers, which are probably of little importance with respect to geothermal exploitation of the Bunter Sandstone Formation. One may argue that sorting of cuttings other than just sieving in order to minimize the content of silt and claystone for the acid titration experiment would have given a better estimate of the carbonate cement in sandstone. However, this kind of sorting would be very time consuming, and there would be little guaranty of a better or more realistic prediction of the formation stability with respect to repeated acidizing job to regain permeability of the perforated zone of the injection well.

In conclusion, cuttings are not suitable material for making estimate of sandstone stability with respect to acid treatment to overcome clogging problems in the sandstone.

3.3 SEM on selected cuttings

The material representing the Bunter Sandstone Formation in the Margrethholm-1 well is rather limited, as only cuttings samples are present. Sand and sandstone fragments (one example illustrated by a red circle in figure 1) were handpicked from washed and dried cut-

tings samples and investigated in stereo microscope and in scanning electron microscope (SEM). SEM investigations of cementing phases, crystal morphologies, dissolution features and paragenetic relationships were performed on gold coated rock chips mounted on stubs using a Phillips XL 40 scanning electron microscope (SEM). The scanning electron microscope was equipped with secondary electron detector (SE), back-scatter detector (BSE); and with a Thermo Nanotracer 30 mm² detector surface window and a Pioneer Voyager 2.7 10 mm² window Si(Li) detector energy dispersive X-ray analysis (EDX) system. The electron beam was generated by a tungsten filament operating at 17 kV and 50-70 µA. Information from cuttings samples are, compared with core samples, subject to several possible errors. When cuttings samples are the only available samples it has to be clear that they may not reveal all the required or necessary information.

Cuttings sample from the depth 2510 m is characterised by loose cemented sandstone fragments and some single grains. Authigenic quartz is a common authigenic phase (Fig. 15A). The sand grains in sandstone fragments are held together by illitic-chloritic clays and minor amounts of authigenic quartz and feldspar (Fig. 15B). Sandstone fragments like these probably have a low survival potential during drilling, and may have been much more abundant than the cuttings samples show.

The cuttings sample at the depth 2535 m is characterised by calcite cemented sandstone fragments. The calcite cement formed at minimum two stages, first as rims of tiny calcite crystals and later as pore filling cement (Figs 15C & 15D). The calcite cement stabilise the sandstone, and removal of this cement will create a loose sediment, as not many other authigenic phases were seen in the calcite cemented sandstone fragments. These intensely cemented sandstone fragments have a higher survival potential than less cemented sandstone fragments.

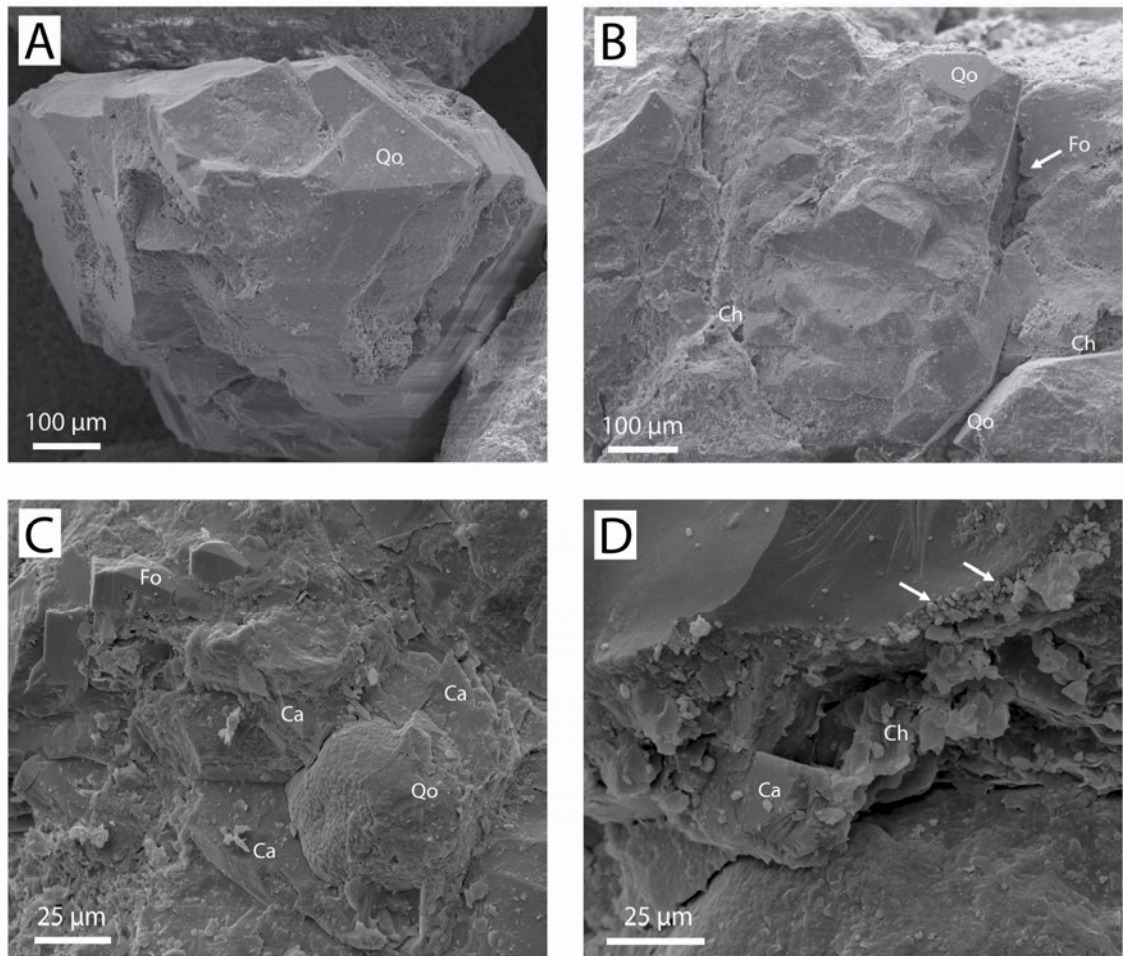


Figure 15. Cuttings samples from the Margrethholm-1 well. A. Quartz overgrowths (Qo) on quartz sand grain, depth 2510 m. B. Sandstone fragments bound together illitic-chloritic clays (Ch), quartz overgrowths (Qo) and K-feldspar overgrowths (Fo). C. Calcite (Ca) cemented sandstone fragment enclosing detrital quartz grain with incipient quartz overgrowths (Qo) and albite overgrowths (Fo), depth 2535 m. D. Tiny calcite crystals (marked by arrows) prior to chloritic-illitic clays (Ch) and late calcite cement (Ca), depth 2535 m.

4. Acid treatment of St19 core sample

The triangular subsample shown in figure 3 was broken into two one of which was to be examined before and acid treatment.

4.1 Record of the acid treatment

A fraction of the subsample weighing 17 g was placed in a 100 cc beaker, and 20 mL of 0.1 molar hydrochloric acid was added. The pH of the solution was determined shortly after showing a pH of 1.4. The core sample was left in solution without stirring and after a few hours tiny gas bubbles were observed on the surface of the sample. With time the bubbles grew in size. After the weekend pH was measured again showing a pH of 7.4. Furthermore, tiny grains were observed on the bottom of the beaker.

Another 10 millilitres of 0.1 molar hydrochloric acid was added while gentle stirring was commenced using a magnetic stirrer. The change in pH was recorded with time, Fig. 15. After almost 20 hours the solution had reached a pH of 5.4 and the experiment was stopped. The core sample was removed from solution and dried. The tiny particles were recovered by filtering the solution. After drying the amount of fine particles was determined by weighing, Table 3.

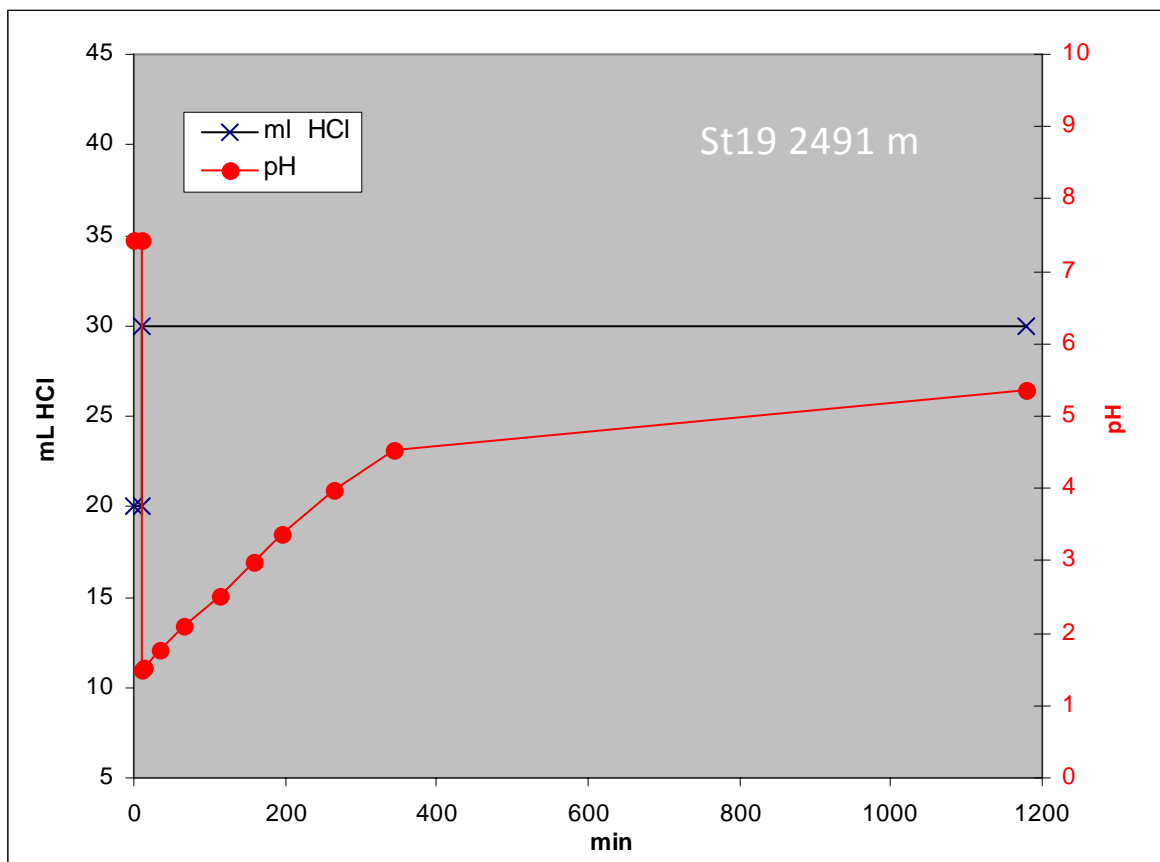


Figure 16. pH change with time after addition of extra 10 mL 0.1 M HCl.

Table 3. Summary of acid treatment of St-19 core, 2491 m

Sample (g)	mL 0.1 HCl	pH start	pH final	duration	"fines"	CaCO ₃
17.7	20	1.4	7.4	70h		
	+ 10	1.5	5.4	20h	0.15 g	150 mg

The amount of CaCO₃ dissolved was calculated assuming all of the acid reacted with CaCO₃

By incident the amount of fines released as a result of acid reaction was the same as the carbonate cement being dissolved by the acid, Table 3.

4.2 Microscopy of core sample

The effect of the acid reaction on St-19 was studied using the simple digital microscope shown in Fig 8. The fine particles released from the St-19 core during acid reaction, most likely due to dissolution of the carbonate cement, were typically 0.1 mm or less in size, Fig. 17. Furthermore, the effect of the acid reaction is illustrated by the micrographs taken before and after acid treatment of the core, Fig. 18.

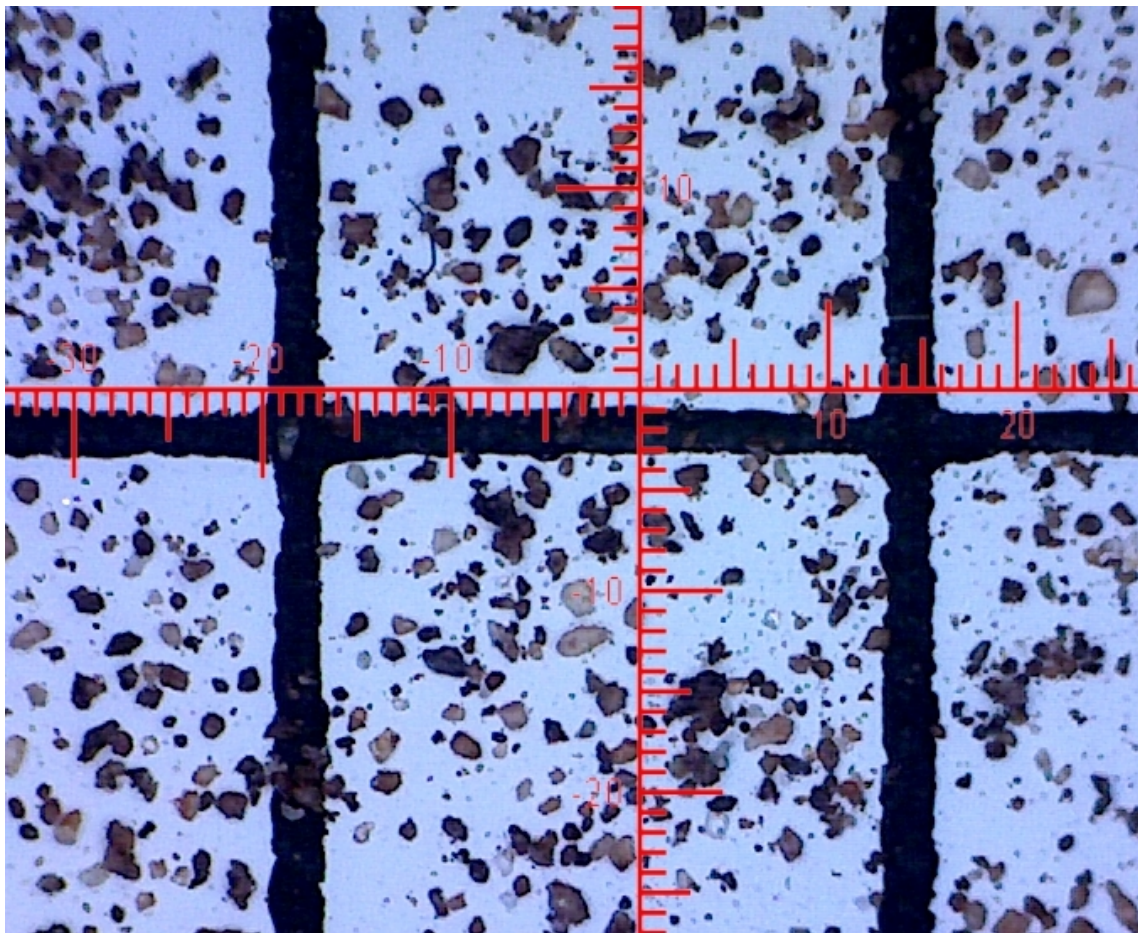


Figure 17. Micrograph of fine material released from St-19 core by carbonate dissolution.

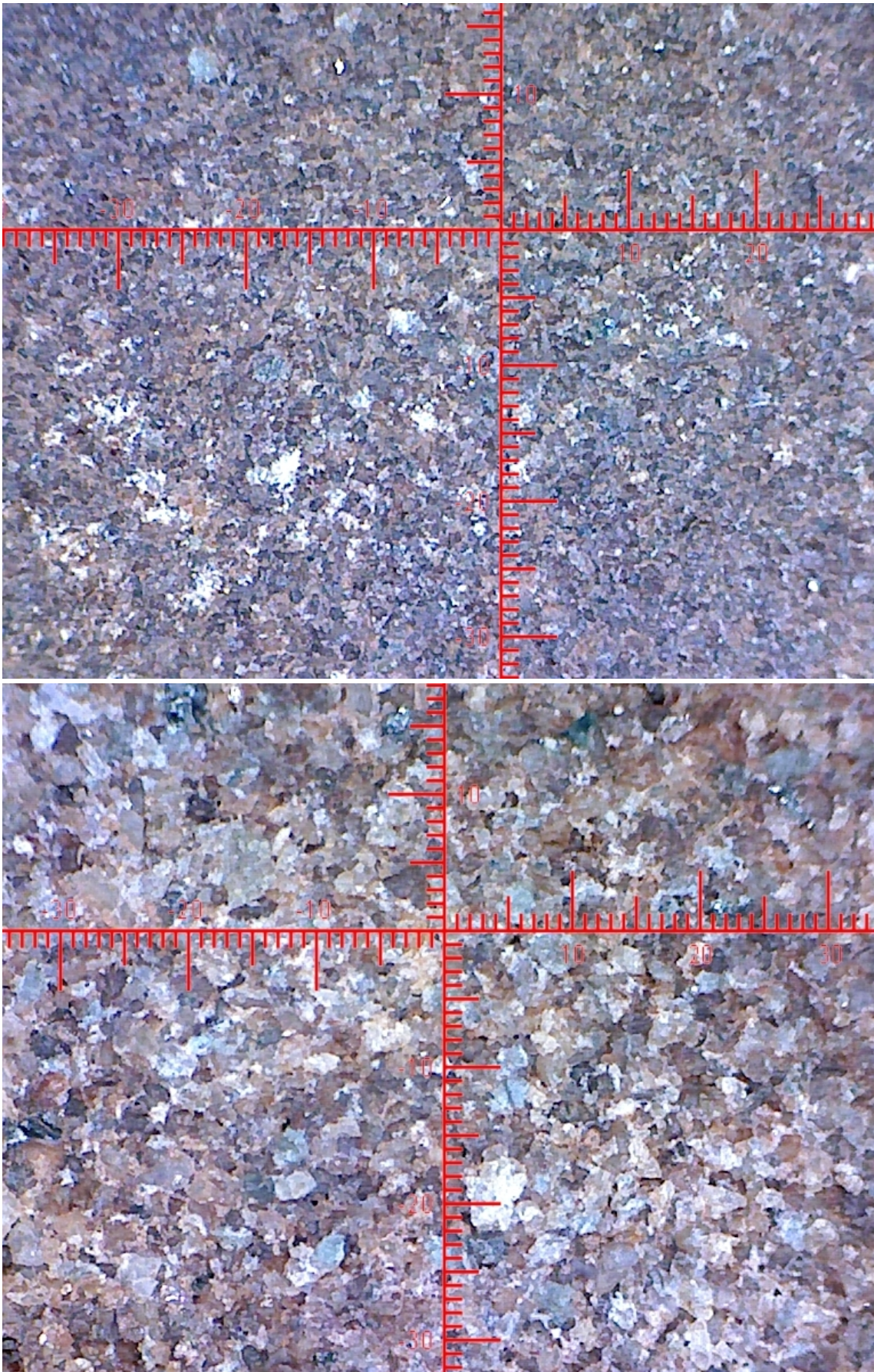


Figure 18. Micrographs of St-19 core before (upper), and after (lower) acid treatment

From the micrographs of Fig. 18 it appears, that the white infilling between the darker grains has disappeared, indicating that the white material consisted of calcium carbonate which had been dissolved by the acid. The occurrence of tiny bubbles observed on the surface of the core mentioned above, most likely consisted of carbon dioxide. The surface of the core after acid reaction also appears to be a little coarser than before.

4.3 Petrography of core material

The petrography of the Bunter Sandstone Formation in the Danish Basin has previously been described in more details /3/ and /4/, here only a very short summary is given. The composition of the Bunter Sandstone Formation is typically arkosic and subarkosic /3/ with a dominance of K-feldspar over minor Na-rich plagioclase. Sedimentary rock fragments are relatively more abundant than igneous and metamorphic rock fragments. Over size clay clasts from overbank strata is typical in ephemeral stream deposits. Detrital carbonate fragments are common in both fluvial and shoreline deposits, and especially ooids are numerous in aeolian sandstones. Re-crystallised shell fragments are common only in shoreline deposits.

The most common porosity reducing authigenic phases are carbonates (calcite and dolomite), anhydrite and clay minerals (illite, chlorite, mixed-layer illite/smectite and mixed-layer smectite/chlorite). Authigenic calcite occurs in several ways; as overgrowths on carbonate rock fragments, as caliche and as pore filling cement. Dolomite occurs as pore filling cement and as rhombohedral-shaped crystals commonly inside clay clasts. Anhydrite may locally, especially in fluvial sandstones and sabkha deposits, be an important porosity reducing cement where it occurs as poikilotopic cement.

4.4 Petrography of the acid treated core samples

Calcite cement is a common authigenic phase in the Bunter Sandstone Formation from the Stenlille-19 well. The calcite cement occurs as pore filling (Figs 19A & 19B). Detrital carbonate clasts are not observed. After acid treatment the pore filling calcite cement is intensively dissolved, actually it is difficult even to find areas where remnants are still present.

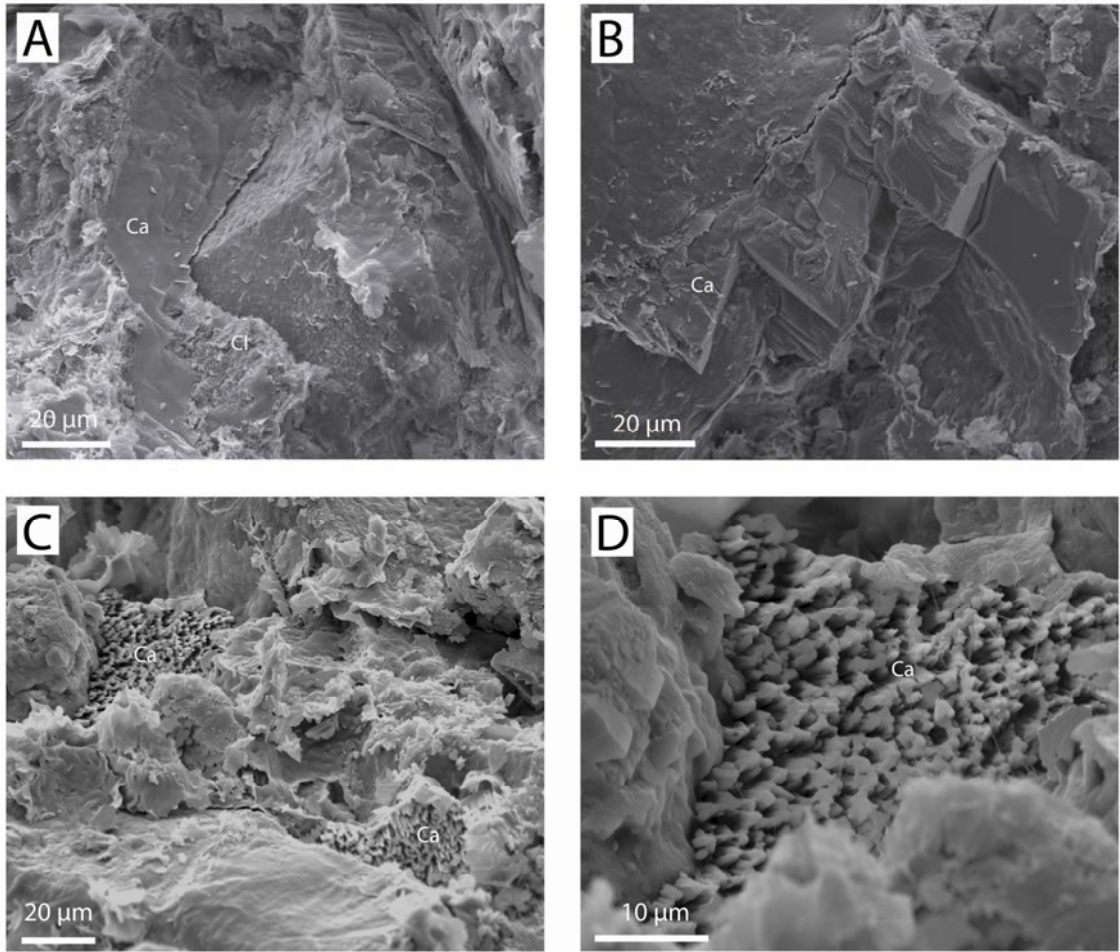


Figure 19. Bunter Sandstone Formation from the Stenillite-19 well, 2491.17 m. A. Calcite (Ca) cement formed after authigenic clay (Cl), untreated sample. B. Calcite (Ca) cemented sandstone, untreated sample. C. Intensive dissolution of calcite (Ca) cement, acid treated sample. D. Intensive dissolution of calcite (Ca) cement, acid treated sample.

5. Summary and concluding remarks

Investigations concerning the possible consequences of repeated acid injections on the stability of the Bunter Sandstone reservoir were performed at GEUS. The studies was initiated after acid injection had been applied to solve problems due to pressure build-up in the injection well of the Margrethholm geothermal plant. Unfortunately, drill cuttings were the only reservoir material available for testing the Bunter Sandstone stability at the Margrethholm site. Meaning that only limited information concerning the local reservoir framework could be established due to the tiny size of the cuttings. Furthermore, cuttings sampled at a particular depth of drilling consist not only of rock from that depth but also material from shallower levels due to caving. Therefore, cutting analyses was supplemented with core studies using core material from the Stenlille-19 well (70 km from Margrethholm) in order to obtain a better judgment of the consequences of acid reaction with reservoir rock. However, judged by the cuttings the most productive intervals of the Margrethholm reservoir appear to be more coarse-grained and less cemented than the sandstone represented by the Stenlille-19 core.

Investigations on cuttings samples from the Margrethholm-1 well:

- Raw material of wet cuttings from 3 levels was washed and cleaned to ensure sufficient material for testing.
- The cleaned and dried cuttings from the producing intervals (determined from the flow log) consisted of a mixture of centimetre sized mudrock clasts and millimetre size sand grains.
- Obtaining representative reservoir material for testing was attempted using a 2 mm sieve assuming larger mudrock clasts to be mainly results of caving.
- Single sands grains (mainly quartz) dominate the sieved cuttings samples from the reservoir interval in the Margrethholm-1 well when viewed under the microscope. Calcite cemented sandstone fragments are rare in the Margrethholm-1 well. Rare quartz cemented sandstone fragments were also present. The rare occurrence of calcite cemented sandstone fragments is considered to reflect the reservoir composition, and not the result of drilling effects.
- Unfortunately, no safe conclusions can be drawn from the rare calcite and quartz cementation concerning the framework stability of the sandstone with respect to acid.
- Microscopic investigation of sieved cuttings prior to and after acid treatment with 0.1 molar hydrochloric acid revealed that much of the acid reaction is most likely due to smaller mudrock clasts also present among the sieved cuttings samples.
- Disintegration of the mudrock clasts among the cuttings indicate that a potential risk of the acid treatment of the reservoir may exist which could result in migration of fines.

Investigations on the core samples:

- Data from deep on-shore wells show that calcite cemented sandstones are common in core samples of the Bunter Sandstone Formation in other parts of Denmark, here even detrital carbonate clasts may occur.

- The core from the Stenlille-19 well had been taken from the upper part of the Bunter Sandstone Formation and may therefore not be representative for the entire reservoir sandstone in the Margrethholm-1 well.
- Acid reaction with the sandstone of the Bunter Sandstone Formation was documented measuring the pH change with time placing core material in a fixed volume 0.1 molar hydrochloric acid. Gas bubbles evolving during the experiment indicate formation of carbon dioxide as a result of acid reaction with calcite.
- Intensely calcite dissolution was documented by scanning electron microscopy after a fairly short exposure of a core sample to 0.1 molar hydrochloric acid solution.

Partial disintegration releasing fine particles from the outer surface of the core sample during the pH monitoring experiment was observed. This indicate that a potential risk exist with respect to mobilization of fines at least locally in the event of acid injection into the Bunter Sandstone Formation, as other authigenic phases appear to be sparse in the calcite cemented intervals.

6. Recommendation

The assumption the calcium carbonate causes the injection problems is primarily based on the positive effect of acidizing. Since cooling increases the solubility of calcium carbonate the precipitation of the substance is most likely due to loss of CO₂ by degassing. For a safer conclusion concerning the exact cause for the injection problems we recommend, that the relative volume of gas released by degassing be determined. The composition of the released gas should also be analysed.

In the event of super-saturation due to CO₂ degassing clogging problems in the injection well may be avoided if calcium carbonate precipitation is catalyzed in a pre-filtering system prior to injection. Precipitation seldom occurs instantaneously in case of weak to moderate super-saturation, a suitable surface is usually necessary to initiate crystallization. We therefore recommend examination of various possibilities to catalyse calcium carbonate precipitation from the geothermal water before filtration and injection.

7. References

/1/ GEUS rapport 2002/95: "Vurdering af udfældningsrisici ved geotermisk produktion fra Margretheholmboringen MAH-1A - Beregning af mætningsindeks for mineraler i saltvand fra Danmarks dybe undergrund"

/2/ BWG (2002) Geochemical investigation of a downhole sample (geothermal well / Denmark).

/3/ Weibel, R. & Friis, H. 2004: Opaque minerals as keys for distinguishing oxidising and reducing diagenetic conditions in the Lower Triassic Bunter Sandstone, North German Basin. *Sedimentary Geology* 169, 129–149.

/4/ Weibel, R., Olivarius, M., Nielsen, L. H., Abramovitz, T. and Kjølner, C. 2010. Petrography and diagenesis of the Triassic and Jurassic sandstones, eastern part of the Norwegian-Danish Basin. Contributions to the EFP-project Aqua-dk. Danmark og Grønlands geologiske undersøgelse Rapport 2010/114, 81p.

8. Appendix A.

Details on injectivity problems and measures taken to solve the problems (mail from J. Magtengaard, DONG Energy October 14th, 2010)

Re: Bunter Sandstone stability against acid: The geothermal plant Margrethholm (at Amager power station) exploits the Bunter Sandstone reservoir. Margrethholm-1 well is being used for injection of geothermal water. We have a strong presumption that calcium carbonate precipitates in the injection well, since problems occur whenever water is not cooled below approx. 20 degrees prior to injection. We observe a slow pressure build-up especially during periods of uneven injection. We have successfully treated the well bore 3 times using a weak solution of hydrochloric acid. The pressure records show a decrease of 20 to 40% within a few minutes after the acid solution reached the perforations, resulting in almost recovery of the initial injectivity.

Acid treatment is considered a success as the presumed calcium carbonate is removed almost immediately.

We have so far been very careful with the amount of acid and the strength of the acid solution, as we know too little concerning the potential risk of removing the cementation of the sandstone. Removing the cement may produce loose sand, which can block perforation. So far we have not seen signs of cement dissolution, but as we foresee that 1-2 acid treatments per year may be necessary, we would like you to evaluate the possible risk of dissolution of the cementation.

We are aware, that we cannot not provide you with drill cores from the very well for further examination. There may perhaps be plugs or cuttings that could be tested. Possibly you could take material from other wells, provided the geology (cementing) is close to being the same

Formation water composition is probably not very important, as long as the salinity is close to what we have on Margrethholm, but we may provide you with a sample if needed.

Hydrochloric acid is added, to maintain pH between 1.5 to 2, which is relatively weak, but apparently effective mixing. In addition, an inhibitor to protect steel pipes in the bore is added. Normally, we treat the well by adding acid using a piston pump located at the surface during injection of 1 to 2 hours. After this, the acid mixture is displaced from the borehole and perforations injecting water without acid.

Plugs may be tested in flow through experiments, but perhaps it may be sufficient to put cuttings in a bath of acid solution and check them before and after. It would be interesting to have a comparison of tests with pH 1, pH 1.5, pH 2 and pH 2.5 (Google translation)

9. Appendix B.

Comments and proposal of work program to study acid susceptibility of Bunter Sandstone (mail from T.Laier, GEUS November 11th,2010)

Your description of the problems with pressure build-up in the injection well and the rapid response upon acid treatment fits well with presumption that the problems are caused by precipitation of calcium carbonate. Also the fact that the problem does not occur when water is cooled down to below 20 degrees further supports the assumption that precipitation of calcium carbonate as the cause, since its solubility is higher at lower temperature.

Your suggestion to study the acid effect of cuttings can probably give a first indication of problems that may arise as a result of break-down of the sandstone. However, the experiments can hardly be performed as simple as you describe, as one has to consider:

- 1) presence of residues of the highly alkaline drilling mud in the cutting samples*
- 2) caving i.e. contamination with material from higher horizons, and*
- 3) difficulties in controlling the pH during the experiments, the pH will change as soon as the acid reacts with rock or drilling mud residue*

The problem of contamination by caving can be partially solved by sorting the dried samples under a microscope, but it obviously takes some time. The content of drilling mud residues may be determined by the acid consumption is needed to change the pH from strongly alkaline to neutral. This could be done by a titration of a suspension of the sample - the same way as you perform the classic acid / base titration. The acid reaction with the rock can also be determined by titration. Just be aware that the reaction is hardly instantaneous, so the rate of acid addition must be adjusted so the pH is not changed drastically. The best way would be to follow the pH variation at an appropriate rate of acid addition, at a pH range which ensures an adequate response rate between acid and minerals. The amount of added acid from neutral to proper acidic pH will give an indication of the "acid sensitivity" of the rock, but only a limited say about which parts - minerals – reacted with the acid.

Rock mineralogy can be determined by XRD X-ray analysis. But to get a better understanding of the various types of cement and if carbonate also exist as detrital grains (which is the case in several places in southern Jutland) we recommend using sidewall cores, so that thin sections before and after titration experiments can be examined. Details concerning the effect of acid reaction with the rock may be obtained by studying polished samples of cuttings under a microscope before and after acidification.

Given the results of the preliminary examinations, various acid flow-through experiments may be decided for side-wall cores.

Finally, the effect of acid treatment may also be studied on core-plugs of the St19 well, located 70 km from Margrethholm.

The experiments mentioned most likely require more material than is available from the quantities of dried cuttings, so there will also be costs due to preparation of starting material from the wet cuttings including the work of a technician for sorting of cuttings samples.

Studies of thin sections of sidewall cores before and after acid treatment is relatively time consuming, so unfortunately we cannot offer to conduct this type of studies this year.

Given the above considerations, we can offer the following two options:

1st Study of acid exposure of sandstone reservoirs using sidewall cores

1a) Cutting of 2 slices of sidewall core, one treated gradually with dilute hydrochloric acid of known molarity (0.1 M ~ pH = 1), with continuous measurements of pH. Any visual changes to the core material will be recorded.

1b) Changes in the sandstone before and after acid treatment will be examined by microscope studies of 2 pcs. thin-sections.

Price: approx. 70 000 kr Point 1a) to be implemented this year and 1b) after the turn.

2nd Study of acid reaction effect on sandstone reservoirs using cuttings

2a) Cleaning and sorting of cuttings in order to avoid caving material, XRD analysis to determine the type of cement present and acid titration experiment as described above, including visual assessment (this year)

2b) Polished sample for the study of acid exposure in microscopic examinations (after turn of the year)

Price 2a) approx. 25 000 kr, 2b) approx. 25 000.

(Google translation)