

How to cook “Strasbourg” sandstone

by Bas den Brok on 11 nov 1993 in Strasbourg

Why make a SYNTHETIC sandstone?

To study the petrophysical properties of reservoir rocks, it is important to be able to vary ONE petrophysical property only, to find out the dependence on this specific property. In nature it is very difficult to find rocks in which only one property varies while other properties remain the same. Rocks are needed in which for example only the grain size, or only the grain shape, the percentage of cement, the composition of the cement, etc., varies.

We wanted to make a synthetic quartz-sandstone with one grain size, one grain shape, shape one grain composition, one cement composition, but with a variable cement content. This cement we wanted to be BRITTLE, i.e., not consisting of an organic substance such as araldite.

Different preparation procedures

Different techniques have been reported in the literature to make synthetic quartz-sandstones with a brittle cement. Amongst these:

Holt and Kenter [1992] made synthetic sandstones by mixing quartz-sand with a solution of sodium silicate and water. After loading the sand-silicate mixture to a given stress state, a proper hardener was injected, causing rapid cementation. By variation of concentrations and mixing ratios, synthetic sandstones could be made that closely resembled reservoir sandstones (according to *Holt and Kenter*, *ibid*). However, they gave no detailed description of the way they make their synthetic sandstones, and they show no optical micrographs of the micro-structure in their paper, nor discuss this in detail. The purpose of *Holt and Kenter* [1992] was to produce synthetic sandstones under stress to study core-damage. They wanted to make synthetic sandstones with a brittle cement similar to that found in real sandstones.

Bernabé et al. [1992] mixed quartz-sand (24-40 mesh Ottawa sand) with a very fine powder of pyrex borosilicate glass (grain size < 10 µm). A small amount of moisture was added during the mixing so that the fine glass particles would stick on the quartz grains and would not segregate due to gravitational forces. Using a uniaxial press the mixtures were pre-compacted at 14 MPa in a carbon mold. Then the mold was heated in a furnace to 950°C while a uni-axial stress of ~0.1 MPa was applied. Under these conditions, the glass particles melted (melting temperature of the

borosilicate glass is $\sim 850^{\circ}\text{C}$). Due to capillary forces, the wetting phase redistributed itself around the grains and particularly at grain-to-grain contacts. After cooling, the aggregate was cemented by a borosilicate glass. Synthetic sandstones were produced with weight volume fractions of glass of 4, 8 and 12% (the porosity was 35.5, 34 and 32% respectively). The major problems with the procedure followed by *Bernabé et al.* [1991] were: (i) the confining pressure during the hot-pressing was too low so that the packing could not be properly preserved at high temperature. Therefore, quartz grains did not touch, but were separated by a thin layer of glass. This can be overcome, however, if a hot-press apparatus is available in which the required P-T conditions can be reached; (ii) lumps of glass were found attached to non-contacting portions of the grains, sometimes forming bridges between neighbouring grains. This problem might be overcome by using a glass with a lower viscosity, thus allowing more complete migration of the melt towards the grain to grain contacts; (iii) the glass particles mixed with the sand might not have been homogeneously distributed as they might have fallen through the pores between the quartz grains to the bottom of the sample.

Visser [1988] reports another way of producing a brittle silica cement, i.e., by reaction of (the highly toxic) SiCl_4 with water (the so-called “silica-lock” method). I will not discuss this procedure here (but see copies attached)

The sol-gel method

We tried a different method. We mixed quartz grains with an alkaline silica-gel to produce silica-gel-coated quartz grains. These gel-coated quartz grains were then hot-pressed above the melting temperature of the silica-gel. The melt moves towards the grain-to-grain contacts and after cooling grains are cemented by a silica-glass cement.

This method has several advantages: (1) the chemical composition of the glass can be varied easily, so that a cement can be obtained with different chemical and mechanical properties; (2) the chemical composition can be chosen in such a way that a relatively low viscosity melt can be obtained at relatively low temperature; in this way the melt might migrate more easily towards the grain-to-grain contacts; (3) the chemical composition can be chosen in such a way that the melting temperature is relatively low so that the experimental procedures are less of a problem; (4) because the gel is coated around the quartz grains, gravitational segregation prior to the melting of the gel is not expected to occur;

We planned to use a silica-gel, so that we would obtain a highly brittle glass cement. To lower the melting point, and to obtain a relatively low viscosity, we originally planned to produce a sodium-potassium-silica gel of eutectic composition. An additional reason to add alkali's to the gel was to make distinction possible between the cement and the quartz grains during scanning electron microscopy (SEM). A sodium-potassium-silica gel of eutectic composition, i.e., 70% SiO_2 , 23%

K_2O , 7% Na_2O , has a melting point of $573^\circ C$ [see *Levin et al.*, 1964]. For reasons to be explained later, we finally decided to produce a cement with a different composition, namely a potassium-silica cement of eutectic composition, i.e., 66% SiO_2 and 34% K_2O , which has a melting point of $\sim 770^\circ C$ [*Wu et al.*, 1993]. I shall first briefly describe how the gel-coated grains were produced, later this will be done in more detail.

We first made the gel. As a silica source we used Tetra-ethyl-ortho-silicate (TEOS). The TEOS was dissolved in ethyl-alcohol. Appropriate quantities of $NaNO_3$ and KNO_3 (as powders) were dissolved in distilled water. Both solutions were mixed, and then appropriate amounts of NH_4OH were added to cause the mixture to turn into a gel quasi instantaneously. Then the right amount of quartz grains were added to the gel, and the mixture of gel and quartz grains was dried.

The gel produced in this way has a high nitrate content, and these nitrates will evaporate at temperatures higher than about $500^\circ C$ (and ambient pressures), i.e., at temperatures below the melting point of the gel. In this way NO_2 -gas will be produced, which is a highly toxic gas. As it is not desirable that a gas is produced during the hot-pressing of the gel-coated grains they were first heated in a furnace (at ambient P) to a temperature high enough to burn off the nitrates completely.

Why we did not produce Na-K- SiO_2 gel but K- SiO_2 -gel

During the heating and de-nitratation of the gel-coated grains at about $500^\circ C$, the Na-K- SiO_2 eutectic aggregate consolidated for reasons not understood, but apparently because the temperature of $500^\circ C$ is very near to the melting temperature ($\sim 0.85 * T_m$). Therefore, bricks were obtained as raw materials for the hot-pressing procedure, and not a loose aggregate. Originally, this was considered no problem, and we envisaged to core cylindrical samples out of these bricks, to put these in carbon sleeves, together with the carbon sleeve into an alumina tube, and this into a furnace placed within a loading frame. The aggregate would then be loaded between alumina pistons at a uniaxial pressure of about 40 MPa and heated to above the melting temperature of the Na-K- SiO_2 gel.

Such a hot-pressing apparatus was not (yet) available in our laboratory, and needed to be built first. Because we wanted to use the synthetic sandstones in experiments in an existing rig at Chevron in Los Angeles (USA), samples needed to have a diameter of about 6 cm and a length of about 12 cm. Therefore, the hot-pressing apparatus to be built needed to be rather large, which was rather inconvenient. Dave Olgaard (from ETH-Zürich), however, suggested later that samples could be hot-pressed in a pressure vessel at their institute. For us this was more convenient than building a new hot-pressing apparatus. However, this also meant that samples needed to be prepared in a different way. The gel-coated grains needed to be available as a powder, and not as a consolidated brick. This powder was then pre-compacted dry in a steel jacket (~ 9 cm diameter, ~ 12 cm long) at a uniaxial load of ~ 50 tonnes after which the steel jacket was weld-sealed.

So, two new problems arose: (i) how to avoid consolidation of the silica-gel coated grains

during de-nitratation at ambient pressure in a furnace, and (ii) we needed to be very sure that no nitrates would be left since a NO₂-gas pressure build-up in the weld-sealed metal capsules during the hot-pressing might result in burst of the jacket.

We decided to avoid this problem by changing the composition of the gel in such a way that the melting temperature would be higher. In this way the gel would not consolidate during the denitratation, AND the denitratation could be carried out at a higher temperature. We choose to make a Potassium-Silica eutectic gel. Now denitrated samples were in the form of a powder, and were denitrated at ~850°C so that any nitrates should surely have been burned off.

Actually, this was another problem: in our laboratory there was no furnace with a controlled atmosphere, and also the composition of any produced gas could not be measured. Furthermore, gases produced during the heating could not be guided away (e.g., in a hood) but freely entered the room. As NO₂ is a highly toxic gas, this was not a very favorable situation. Another disadvantage was that the furnace was too small for the quantities that needed to be prepared.

Details about the cooking of the sandstone

List of chemicals used:

KNO₃ (salpeter)

Molar weight: 101 g
density: 2.109 gcm⁻³
solubility: 13 g/100cc cold water
Rectapur/Prolabo Code article 26 863.291 (purity 98%)

NaNO₃ (sodaniter)

Molar weight: 85 g
density: 2.261 gcm⁻³
solubility: 92 g/100cc cold water
Rectapur/Prolabo Code article 27 950.298 (purity 99%)

Tetraethyl Orthosilicate (TEOS)

Molar weight: 208.1 g
density: 1.05 gcm⁻³
Rectapur/Prolabo Code article 24 006.296

I will give the calculations here of the composition of the KNO_3 -Silica gel which was finally used for the production of the samples. The question is: how much KNO_3 -powder needs to be added to 100 ml TEOS to produce a eutectic composition of 34 mole% K_2O en 66 mole% SiO_2 . In this case, 34/100 mole K_2O , i.e., 68/100 mole KNO_3 should be mixed with 66/100 mol SiO_2 . One mol KNO_3 has a weight of 101 g, 0.68 mole KNO_3 therefore has a weight of $0.68 \cdot 101 = 68.68$ g. One mole TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) has a weight of 208.1 g, hence, 100 ml TEOS, which has a weight of 105 g is equal to $105/208.1 = 0.505$ mole TEOS, i.e., 0.505 mole Si. This means that 1 mole Si is equal to $100/0.505 = 198.020$ ml TEOS. Hence, 0.66 mole TEOS (or SiO_2) is equal to $0.66 \cdot 198.020 = 130.69$ ml TEOS. Hence, 68.68 g KNO_3 needs to be added to 130.69 ml TEOS, or, 52.6 g KNO_3 to 100 ml TEOS

Production of the gel

The gel was produced in the laboratory of the department of geology (Rue Blessig) and not at the IPG since a hood was required, mainly because large quantities of ammonia solution evaporated while drying the gel. The procedure was more or less the same as the one of Prame Chopra (see appendix) which we shall here describe in detail:

The required amount of KNO_3 should be measured and mixed with just as much distilled water as required to dissolve it completely at NPT conditions in a small pyrex beaker. A plastic foil is put over it to avoid evaporation of the water. It is important not to add more water. In that case no good gel is obtained. The mixture is stirred using a small magnetic-stirrer. The solution is heated (60-80°C) while stirring so that KNO_3 will dissolve faster (be careful that the plastic foil doesn't melt). The solution should be stirred at least 1 hr. This is VERY important. If the solution is not well stirred, i.e., the KNO_3 not completely dissolved, the composition of the gel is not the one desired.

Then the required amount of TEOS should be mixed with ethyl alcohol in a pyrex beaker (5 l). A plastic foil is put over it to avoid evaporation of the mix. An ~5 cm long stirring-magnet is used and the mixture at least 30 minutes stirred on an automatic stirrer. Good mixing is again VERY important. When NOT mixed properly, no good gel is obtained. As soon as the KNO_3 is completely dissolved, the solution can be added to the TEOS-alcohol mixture in the 5l-beaker under continuous (automatic) stirring. Some gelling usually occurs and the mixture gets a milkish white colour. After continued stirring the mixture remains milkish white but with very low viscosity. This mixture should be stirred for at least another 0.5 hr (again VERY important!). The plastic foil should still cover the beaker.

Then, the plastic foil may be lifted up a little bit and the ammonium solution added to the solution. Stirring during the addition is important. The mixture quickly turns into a stiff porridge-like gel too stiff for the automatic stirring tool. The magnetic stirring tool can then be turned off and the sand added while stirring by hand with a spoon until an egal porridge-like mixture is obtained.

The viscosity of the gel decreases somewhat during this mixture with the sand. The plastic foil is removed and the beaker placed in an oil bath at a temperature of 70-90°C overnight to evaporate the ammonia, the water, and the ethyl-alcohol. Make sure that the temperature is not higher than 100°C because the mixture will boil then and cause spattering PLUS separation of phases, i.e., sandgrains will end up down in the beaker and a non-gelly low-viscosity liquid on top of the gel. The same is true when the 5 l beaker is heated on a plaque chauffante because then a large temperature gradient develops. Heating in an oil-bath is therefore essential (OR in an oven UNDER a hood).

DO NOT add too much ammonia because then no stiff gel is obtained, and the sand grains will fall down on the bottom of the beaker.

After evaporation of ~12 hr, a whitish powder is obtained. This should be completely dry. If not, and stored in a closed bottle or box, then alcohol remains present and when the gel is heated later in order to evaporate the remaining nitrates, and if the heating is too fast, then the alcohol burns (rather than evaporates) and Carbon particles are produced. This is not desirable. Therefore it is VERY important to dry the gel very good.

So, what we actually mixed was:

100 ml	TEOS
400 ml	Ethyl-alcohol
52.6 g	KNO ₃
139 ml	water
100 ml	NH ₄ OH (Rectapur/Prolabo, Ammonia solution about 32%)

Hence, 739 ml liquid. These quantities together produce 54.74 g (devitrified) glass. We wanted to make sandstones with two different quantities of glass cement, therefore we added 310.19 g SiO₂-sand-grains to make 15 vol% cemented material, and 1040.06 g SiO₂ -sand-grains to make 5 vol% cemented material.

Burning off the nitrates:

Nominally, nitrates should be burned-off at least at 500°C. During heating in a furnace at 860°C usually the volume of the gel-powder decreases about 10-20%. It is not sure whether this is entirely due to the de-nitratization. In case of the 5%-cement content K₂O-SiO₂-gel samples, at 860°C, the gel-sand mixture solidifies to a very porous, weakly cemented sandstone. Because for the hot-isostatic-pressing procedure we needed a loose sand aggregate, the sandstone samples were crushed by rubbing the samples weakly against each other. In this way they easily turned into loose sand. Of course this needs to be done very careful because destruction of the individual sand grains is undesirable.

In case of the 15% gel coated sand, heating at 860°C produces a very porous but relatively strong

consolidated sandstone. Simple rubbing of the samples against each other is not enough to produce a loose sand aggregate. Therefore, the mixture was heated to 560°C only. THEN the aggregate did consolidate weakly and it was easy to decompose it into single grains. Because we were not sure that in this case all of the nitrates were evaporated we heated the mixture twice to 560°C. Samples were at least two times for 2 hrs at that temperature. To test whether all of the nitrates were indeed burned off we tried to dissolve a part of the 15% gel-coated sand in water at 90°C and then evaporated the water and tried to see whether there was a crystallised residue with needles with the shape characteristic for KNO₃. This appeared NOT the case, suggesting that no nitrates were left. Nevertheless one should be sceptic about this test and think of other means of testing whether nitrates remained present in this material.

Details about the furnace: (see appendix)

Given the required size of the samples, that needed to be prepared, i.e., ~12 cm long at least, and ~6 cm in diameter, a larger furnace was needed, but there was none. The furnace volume that could be used was about 20 cm long and 7.5 cm high and 12 cm wide, and over this volume there was a gradient of about 100°C at least (see figure in appendix). The gel-powder was heated in a porcelain over dish, about 19 cm long, 10 cm wide, and 7 cm high. During the heating of the nitrate-bearing gel which needed to be done to burn off the nitrates, NO₂-gas is probably liberated. This is highly toxic (see appendix attached). Ideally a furnace with a hood is therefore needed.

Note that the porcelain oven dish cannot stand temperature gradients larger than about 300°C. Therefore, the furnace could not be opened during the heating. We had to wait till the furnace was cooled down to about 250°C before the over dish could be safely removed. Cooling down of the furnace from about 800°C to 250°C takes about 6 hours. The procedure was therefore very time consuming. The room in which the furnace was placed could be very well ventilated. We tried to avoid, however, that people entered the room while NO₂ was (eventually) liberated.

It is advisable in future to (i) use a BIG furnace, so that all the material can be heated in once; (ii) to make sure that the produced NO₂-gas causes no harm, e.g., by placing the furnace under a hood or by ensuring very good ventilation, and (iii) use a furnace with a controlled atmosphere, e.g., so that heating might be carried out in a N₂-flush or in a vacuum which will promote the burning off of the nitrates so that the temperature can remain relatively low (to prevent consolidation of the gel-coated sandgrains)

Hot-isostatic-pressing:

The powders were poured into steel cans of ~9 cm diameter and 12 cm high. This was done in two times and the powders compacted at a load of ~50 tonnes. Not much compaction occurred. The steel cans were then welded and compacted.

Regarding the PT-path: first the pressure was raised to 40 MPa, then the temperature to 800°C. The samples were then hold at these P-T conditions for 1 hr, then lower the temperature to 500°C and then the temperature and the pressure together in one to two hours. (NOTE that I do not know yet whether P and T were actually released in ONE or TWO hours >> see chartrecorder output that goes with the canisters).

Originally we planned to make TWO different batches: a ~5 vol% cement, and a ~15 vol% cement aggregate. But we decided NOT to make the 15 vol% because we found it too risky that this material had only been heated to 560°C and not to 800°C in order to burn off the nitrates so that nitrates still might have been present and might have caused the sample capsules to burst during the hot-pressing at 800°C. Instead, we decided to hot-press two canisters with the ~5 vol% gel coated sand and another with a mixture of 1 part non-gel-coated sand with 2 parts of the ~5 vol% gel coated sand resulting in ~3 vol% cemented sand. Note that in canister 1 and 2 there is the batch with the ~5 vol% cement, and in canister 3 and 4 there is the batch with the ~3 vol% cement.

Microstructure of non-compacted aggregate

We studied thin sections of the material consisting of approximately 5 vol% Sodium-Potassium-Silica-eutectic gel heated in a furnace at ambient pressure and 860°C. (See photomicrographs in appendix.) Because this material was NOT hot-pressed, it had a very high porosity and grains-to-grain contacts were locally observed to consist entirely of a glass phase. The melt, however, appeared to have migrated in most cases towards the grain to grain contacts. Isolated pockets of melt are also present.

Effect of water on the gel-cemented sandstones

Contact with water should be avoided as much as possible because this might cause devitrification of the potassium-silica-glass. We tried to test whether NON-compacted samples of the synthetic potassium-silica-gel cemented sandstone could be cored and sawed in the presence of water. This appeared to be no problem, but we do not know what is the effect on the cement. However, drying of the cored samples on a plaque chauffante at a temperature of approximately 200°C caused that the samples stuck onto the plaque chauffante, so apparently, at those temperatures some of the

potassium-silicate dissolved in the water and precipitated at the contact with the plaque. The samples were then “glued” VERY strongly on the plate and could not easily be removed. If possible, samples should be sawed, cored (and thin sections be made) using “evaporating oil” as a cooling liquid rather than using water since the effect of water on the glass is not well known.

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List of appendices:

- Temperature gradient over the furnace
- Na₂O-K₂O-SiO₂ phase diagram after *Levin et al.* [1964]
- Paper of *Wu et al.* [1993]
- Gel-recipe after Praeme Chopra (pers. comm.)
- Encyclopedie des gaz: relevant chapter about NO₂
- Photo-micrographs of 5 vol% Na-K-SiO₂-gel non hot pressed sample
- Paper of *Roy* [1969]
- Paper of *Hamilton & Henderson* [1968]
- Paper of *Holt & Kenter* [1992]
- Paper of *Bernabé et al.* [1992]
- Relevant chapter from *Visser* [1988]