The Effect of Acrylic Gel Grouting on Groundwater in Porous Media

S. Wagner, C. Boley, Y. Forouzandeh

Abstract—When digging excavations, groundwater bearing layers are often encountered. In order to allow anhydrous excavation, soil groutings are carried out, which form a water-impermeable layer. As it is injected into groundwater areas, the effects of the materials used on the environment must be known. Developing an eco-friendly, economical and low viscous acrylic gel which has a sealing effect on groundwater is therefore a significant task. At this point the study begins. Basic investigations with the rheometer and a reverse column experiment have been performed with different mixing ratios of an acrylic gel. A dynamic rheology study was conducted to determine the time at which the gel still can be processed and the maximum gel strength is reached. To examine the effect of acrylic gel grouting on determine the parameters pH value, turbidity, electric conductivity, and total organic carbon on groundwater, an acrylic gel was injected in saturated sand filled the column. The structure was rinsed with a constant flow and the eluate was subsequently examined. The results show small changes in pH values and turbidity but there is a dependency between electric conductivity and total organic carbon. The curves of the two parameters react at the same time, which means that the electrical conductivity in the eluate can be measured constantly until the maximum is reached and only then must total organic carbon (TOC) samples be taken.

Keywords—Acrylic gel grouting, dynamic rheology study, electric conductivity, total organic carbon.

I. INTRODUCTION

EXCAVATIONS are usually at a depth where groundwater is present, so a way must be found to keep it away from the excavation. If the surrounding soil consists of a layer of sand, the pores of the sand specify the maximum solid particle size of the grouting material. In the past, sodium silicate was one of the used grouting materials, but because of causing high pH values, it is harmful for the environment, and therefore, it is not used anymore. The need for the development of a new, eco-friendly and economical acrylic gel is thus given. At this point the study begins.

Acrylate gels are multi-component grouting materials which consist of monomers that react with a catalyst via a polyreaction to form chemical chains. These chains form a network of what ultimately determines the properties of the gel [1], [2]. In the beginning they have an initial viscosity comparable to that of water. Over time, the flow behavior of

the injection material changes, which has an impact on the pumpability. The pumpability is no longer given when the gel point is reached, which can be determined by rheometric studies. The storage modulus, which reflects the elastic response of the gel, is considered to be a crucial criterion for the gel strength and thus, the permeability behavior of grouting materials [3]. This can also be determined with a rheometer.

When injecting into aquifers, it must be ensured that the water is displaced without the grouting material mixing too much with the groundwater [4]. Therefore, the environmental impact must be considered. Based on the results of the rheometric investigations, reverse column experiments were carried out to investigate the effects of acrylic gel groutings on groundwater and in particular on the measuring parameters pH value, turbidity, electric conductivity (EC) and TOC. In the end, a correlation between EC and TOC was visible.

II. MATERIAL

The polymer gel used in this study is a poly(methyl methacrylate) formed by a radical polymerization of monomers and an initiator solution. The monomer part consists of two components with fixed mixing ratios which have to be mixed before the initiator solution will be added. Initiator solutions with concentrations of 0.14%, 0.17%, 0.43%, 0.50%, 0.71% and 0.83% (by weight) were examined. This resulted in 6 mixing ratios of 1:6.67, 1:5.72, 1:6.69, 1:5.74, 1:6.71 and 1:5.76.

III. DYNAMIC RHEOLOGY STUDY

A. Method

A dynamic rheology study with an Anton Paar rheometer MCR 102 was conducted to determine the time at which the gel cannot be processed anymore and the maximum gel strength is reached. If a rheometer is operated with oscillatory shear, the elastic and plastic response of the gel can be measured as functions over time. The elastic response is the storage modulus (G') which is the mechanical energy stored by the system and the plastic response is the loss modulus (G'') which stands for the loss of heat energy [5], [6]. The intersection of storage modulus (G') and loss modulus (G'') is the end of the processing time [7]. The maximum gel strength was characterized by the storage modulus at the end of the gelation. Examined were different initiator solution concentrations to control the reaction speed and also to examine differences in gel strength.

Before each test, the heating plate was heated up to 20 °C

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and was kept constant during the experiments. After the application of the different mixing ratios, the oscillatory shear with constant amplitudes and constant frequency of 10 Hz was started. The intersection of storage and loss modulus was the time at which mineral oil was applied around the cone to prevent the gel of drying out starting from the edge of the cone. This would lead to higher maximum storage modulus values than can realistically be expected after an injection. The measurements were carried out for up to 12 hours.

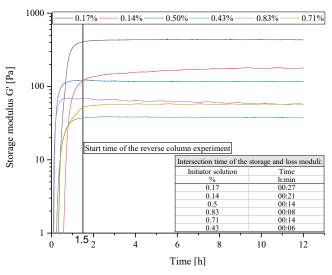


Fig. 1 Storage modulus trend of the gel with different initiator solution concentrations at 20 $^{\circ}\mathrm{C}$

B. Results

To assess the evolution of gel strength over time, the storage modulus profile was examined in more detail (Fig.1). As soon as the gel point has been reached, the course increases rapidly until it reaches a certain height. Then it went into an almost horizontal course. The different mixing ratios with their associated initiator solution concentrations have reached the gel points at a measuring temperature of 20 °C at the times listed in Fig. 1. These are related to the maximum storage modulus after 12 h of measurement. The faster the reaction rate until reaching the gel point, the lower the maximum final storage modulus values. If the initiator solution concentrations are compared with the same amounts of salinity but different water content, higher water content shows a reduction in the maximum gel strength.

IV. REVERSE COLUMN EXPERIMENT

A. Method

To examine the effect of acrylic gel grouting on groundwater a reverse column experiment was conducted (Fig. 2). A 45 cm column packed with 5 cm filter material at the top and the bottom and 35 cm sand in between, which was compacted with 10 hammer blows from each side, was rinsed for 12 hours with a flow of 1.44 l/h to flush out all possible contaminants. The flow direction of the Munich tap water was from the bottom to the top. After stopping the purge without

draining water from the cylinder the injection of 1.4 l was done from the side with constant pressure. The flushing of the cylinder was restarted after 1.5 h which corresponded to the achievement of the gel point of the initiator solution 0.17% by a factor of 3 and the maximum storage modulus value was reached at almost all mixing ratios to 90%. This is considered sufficient to produce an impermeable specimen and to examine only the surrounding of the injection body. The eluate was examined constantly for pH value, electrical conductivity and turbidity using a multimeter handheld device HI 9829 (HANNA instruments).

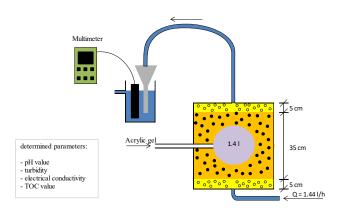


Fig. 2 Flow chart of the reverse column experiment

The pH value is a measure of how acidic or alkaline an aqueous solution is [8]. The electrical conductivity is a sum parameter which reflects the ion concentration. Samples for TOC determination were taken at intervals. Due to better reproducibility, it was decided to use sand as filling material. In sand, only low viscous materials can be injected.

B. Results

The laboratory tests related to the effects on groundwater have shown that there is nearly no change in the natural pH values (+/-0.15) or turbidity (+0.2 FNU) but there is a dependency between EC and TOC (Fig. 3).

In Fig. 3, the electrical conductivity values and the TOC values were calculated with the maximum measured values and plotted over time. If the time axis is used as a mirror axis, it is noticeable that the gradients are very similar to each other. The beginning of the increase and the maximum value reached take place at nearly the same time. In order to better compare the two processes, both the TOC values and the electrical conductivity values were described with the following equation according to Boltzmann:

$$y = A2 + \left(\frac{A1 - A2}{1 + \exp((x - x_0) / dx)}\right)$$
 (1)

where AI = initial value; A2 = final value; and x = time; x_0 = center; and dx = time constant.

As can be seen in Tables I and II, the time of reaching the turning point (center) in the TOC curves is always reached

slightly after reaching the electrical conductivity values. This is due to the locally slightly different measuring point. If one considers the percentage difference of the final EC and TOC values of the mixtures with the same water content, the gradient is decreasing. This also can be seen in Fig. 4. The maximum values were plotted and only the measured values with the same water content were connected. The values can be described by an exponential function, which reads as follows:

$$y = y0 + A * \exp^{(R_0 * x)}$$
 (2)

where y0 = offset; A = initial value; $R_0 = rate$; and x = crosslinker concentration.

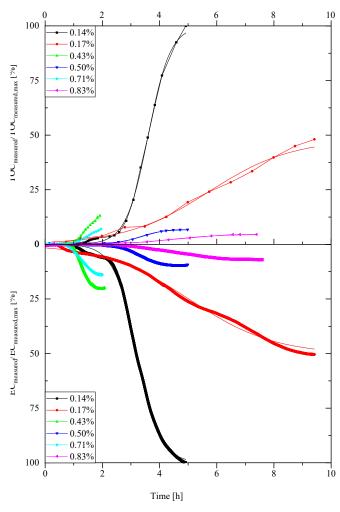


Fig. 3 Eluate measurement results of EC and TOC of the different initiator solution concentrations

The functional values are shown in Table III. The diagram shows that the percentage difference of the two measured parameters is smaller with higher water content and identical salinity but when comparing the rate of the exponential functions, higher water content means a bigger difference (7.94% compared to 5.59%). This means that with mixing ratios with less water content, the rate of the curves will flatten

and the low salt values will match those of the high salt values. To confirm this statement further laboratory experiments must follow. For salinities with the same amount of water the EC and TOC values can be read from Fig. 4.

TABLE I REGRESSION PARAMETERS FOR THE EC VALUES

Initiator	0.14	0.17	0.43	0.50	0.71	0.83
solution			%			
A1	0.0	0.0	0.0	0.0	0.0	0.0
A2	100.0	50.5	20.5	9.6	13.9	7.0
x0	3.2	5.0	1.3	3.3	1.3	4.4
dx	0.4	1.5	0.1	0.3	0.2	0.8
Adj. R-Sq.	0.999	0.994	0.999	1.000	0.997	0.997

TABLE II

REGRESSION PARAMETERS FOR THE TOC VALUES							
Initiator	0.14	0.17	0.43	0.50	0.71	0.83	
solution			%				
A1	0.0	0.0	0.0	0.0	0.0	0.0	
A2	100.0	48.1	13.1	6.7	7.0	4.5	
x0	3.6	5.7	1.4	3.3	1.4	4.4	
dx	0.4	1.5	0.2	0.4	0.2	0.8	
Adj. R-Sq.	0.998	0.990	0.995	0.992	0.996	0.985	

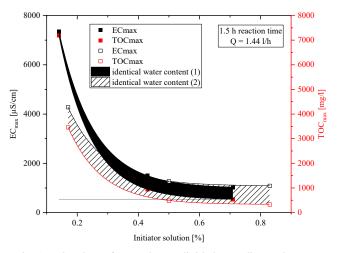


Fig. 4 Peak values of EC and TOC divided according to the same water content with (1) higher and (2) less based on the total mixture content

TABLE III
EC- AND TOC-FUNCTION VALUES DIVIDED ACCORDING TO THE SAME
WATER CONTENT

Water	(1)	(2)		
content	EC	TOC	EC	TOC	
y0	980.0	498.78	1071.86	317.65	
A	21545.78	25082.30	13462.31	14363.2	
R_0	-8.69	-9.44	-8.45	-8.95	

V. CONCLUSION

The rheological measurements were used to determine the gel point as well as the storage modulus profile of the 6 mixing ratios. The attainment of the gel point was the prerequisite for the start of the flushing of the reverse column experiment. At this time, 90% of the maximum storage

modulus of the mixing ratios (except with the initiator solution 0.14%) was reached. This was considered impermeable.

In the reverse column experiment, the parameters pH value, turbidity, EC and TOC values were determined after the injection of the mixtures. While the former parameters showed little change, the trend of the electrical conductivity and the TOC content were similar. The conclusions are as follows:

- Maximum values are reached at the same time
- The slope of the electric conductivity and TOC adjustment curve decreases with increasing initiator solution
- Less water content means a lower slope in the beginning of the curve
- Less water content means a bigger difference between EC and TOC values
- EC and TOC values of mixtures with the same amount of water but different salinity can be read out of Fig. 4

Our results show that as the electrical conductivity, which returns the ion concentration, increases, so does the TOC content. The maximum value is reached at the same time. In practice, this means that with this material the electrical conductivity of the eluate can be measured constantly and when the maximum value of the electrical conductivity is reached, a sample can be taken for the determination of the TOC value. This laboratory experiments were conducted with a flow of 1.44 l/h. For other flows further research must be done. A connection between storage modulus and difference between EC and TOC values could not be found.

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REFERENCES

- S. Koltzenburg, M. Maskos, O. Nuyken, *Polymere:Synthese, Eigenschaften und Anwendungen*. Berlin, Heidelberg: Springer Spektrum, 2014.
- [2] S. Weber, H. Schäffler, E. Bruy, G. Schelling, *Baustoffkunde*. vol. 10, Würzburg: Vogel, February 2012.
- [3] C. A. Grattoni, H. H. Al-Sharji, C. Yang, A. H. Muggeridge, R. W. Zimmerman, "Rheology and Permeability of Crosslinked Polyacrylamide Gel," *Journal of Colloid and Interface Science*, vol. 240, July 2001, pp. 601-607.
- [4] C. Kutzner, *Injektionen im Baugrund*. Stuttgart: Ferdinand Enke, 1991.
- L. Gehm, *Rheologie*. Hannover: Vincentz, 1998.
- 6] G. Schramm, Einführung in die Rheologie und Rheometrie. Karlsruhe: Gebrüder HAAKE GmbH, 1995.
- 7] T. G. Mezger, Angewandte Rheologie. Graz: Anton Paar GmbH, 2014.
- [8] W. Kölle, Wasseranalysen richtig beurteilt. Weinheim: WILEY-VCH, 2010