GROUTING BY CONTROLLED GYPSUM CRYSTALLIZATION FROM SUPERSATURATED SOLUTIONS – A NEW WAY TO REDUCE BRINE INFLOWS INTO SALT AND POTASH MINES

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1. Introduction

The Mosaic K2 Esterhazy potash mine has been successfully controlling an inflow of brine since 1985. Inflow rates have averaged about 3,500 gallons per minute (gpm), or nearly 0.2 cubic meter per second (m^3/s). The inflows originate from the fractured Dawson Bay formation overlying the mine. The Dawson Bay formation consists of dolomite, limestone and minor beds of anhydrite and mudstone. The inflows are typical sodium chloride (NaCl) brines with sulfate concentrations of 0.2 to 0.3 wt.-%.

Inflows have been controlled by injecting concentrated calcium chloride ($CaCl_2$) solutions into the Dawson Bay formations. When $CaCl_2$ solutions mix with Dawson Bay brine, gypsum ($CaSO_4 \cdot 2H_2O$) and in some cases sodium chloride (NaCl) crystallization occurs ahe flow paths become restricted as the gypsum grows on the wall of the fracture. Historically, this approach has proven to be very effective at controlling inflows. However, the mixing required between the $CaCl_2$ solution and the Dawson Bay brine to cause gypsum precipitation in the fractures is not always achieved. For example in some situations, plug-type flow may be dominant resulting in little to no flow reduction even though high concentrations of calcium chloride are present in the inflow. This problem can be overcome by using supersaturated gypsum solutions as grout. These solutions contain calcium sulfate in concentrations above the normal solubility of gypsum. The stability of these supersaturated gypsum solutions can be controlled, therefore allowing the crystallization of gypsum in flow paths without any mixing with Dawson Bay brine.

The paper summarizes the fundamentals of the technology and gives an overview of the field tests that have been performed.

2. Mosaic Potash Esterhazy Operation

The Mosaic Company, headquartered in Minneapolis, Minnesota, is one of the world's leading producers and marketers of concentrated phosphate and potash crop nutrients. Mosaic's

Esterhazy operation, which is located in Saskatchewan Canada, is the largest potash mine in the world. The mine is located approximately 213 km east of Regina, Saskatchewan and 430 km west of Winnipeg, Manitoba. The mine began operation in the 1960's and employs over 800 people. The ore deposits, which are located at a depth of 960 meters, are believed to be the richest and largest in the world. The mine has two surface mills located ~10 km apart and the mining area is approximately 30 km by 20 km at the present time.

For over 20 years the Esterhazy mine has successfully controlled an inflow of NaCl saturated brine entering a small section of the mine. The injection of calcium chloride, which causes the precipitation of gypsum, has proven to be very effective in dealing with excursions and maintaining the inflow at an average of 3500 US gpm or less. In an attempt to further reduce the inflow and/or permanently stop the inflow an extensive research program into alternate grouts and grouting technologies was undertaken.

The NaCl saturated brine comes from the Dawson Bay formation, a major aquifer locally, which is separated from the top of the Prairie Evaporite by the relatively thin shale of the Second Red Bed. The Dawson Bay formation is on the order of 160 ft thick and the Second Red Bed is approximately 30 ft thick. The thickness of salt between the mined openings in the Esterhazy ore zone and the top of salt (i.e., bottom of the Second Red Bed) is approximately 75 to 100 ft. The Dawson Bay formation is primarily a carbonate sequence com-posed of limestone and dolomite. Regionally, the Dawson Bay formation is not considered to be a major prolific aquifer; however, in the K2 area, the lower section of the Dawson Bay formation is highly fractured. The fractured lower section collects water over a larger area from the porous upper section and conveys it under the inflow induced hydraulic gradient toward the mine inflows.

3. Fundamentals of using gypsum crystallization processes from supersaturated solutions for grouting of brine inflows

Almost all salt minerals are highly soluble. Gypsum and anhydrite are the only minerals with low solubility, if complex salt minerals such as syngenite or polyhalite are neglected. Anhydrite ($CaSO_4$) is the thermodynamically stable calcium sulfate mineral in saturated NaCl brine at 25 °C. Its formation, however, is kinetically impossible at low temperatures and gypsum is formed instead of anhydrite. Because the absolute differences of the solubility's between the two salts are small, gypsum can be regarded as the quasi stable component.

Fast and almost quantitative gypsum formation takes place when $CaCl_2$ and magnesium sulfate ($MgSO_4$) solutions are mixed. This process can be controlled by the addition of precipitation inhibitors, therefore preventing the spontaneous precipitation of gypsum. Clear, supersaturated solutions are obtained with a known stability (Figure 1). Gypsum crystallization can be controlled over a period of few minutes to several hours, depending on the degree of supersaturation and the relative inhibitor content.

Isothermal stirring experiments at 25 °C were carried out in order to determine the timely course of gypsum crystallization in NaCl saturated solutions. The change in the calcium concentrations of the solutions served as an indicator for the course of crystallization. Complexometric titration with EDTA was used for their analytical determination. NaCl saturated solutions containing $CaCl_2$ or $MgSO_4$ were prepared by the dissolution of $CaCl_2*2H_2O$ and $MgSO_4*7H_2O$, respectively, in NaCl brine. A dilute solution of inhibitor was added to the calcium or sulfate solution before mixing the two to form the grout.

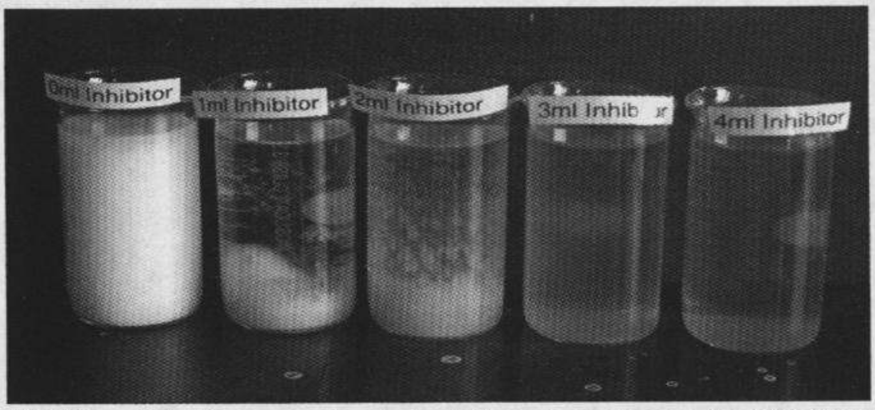


Fig. 1: Stability of $CaSO_4$-supersaturated solutions depending on the inhibitor content

Figure 2 shows the course of gypsum crystallization depending on the salt content of the solution. Increasing NaCl concentrations result in solutions with lower stability. This means that stabilization of the same $CaSO_4$ supersaturation in saturated salt brine requires higher inhibitor contents than in water. As Figure 3 indicates, the stability of the solutions depends on the inhibitor content. Higher inhibitor concentrations give solutions with higher stability. In many cases the use of a mixture of inhibitors is favorable. Figure 4 summarizes how the course of crystallization can be directed by changing the ratio between the two inhibitor components. The addition of inhibitor B results in an increase of the short term stability of the solution. Complete gypsum crystallization takes place within 24 hours. If these supersaturated $CaSO_4$ solutions come in contact with rock, gypsum will gradually precipitate in layers (Figure 5). In the case of penetrating a fracture, step by step closure takes place. A simple sketch of the application of gypsum forming grouts to seal flow paths is given in Figure 6.

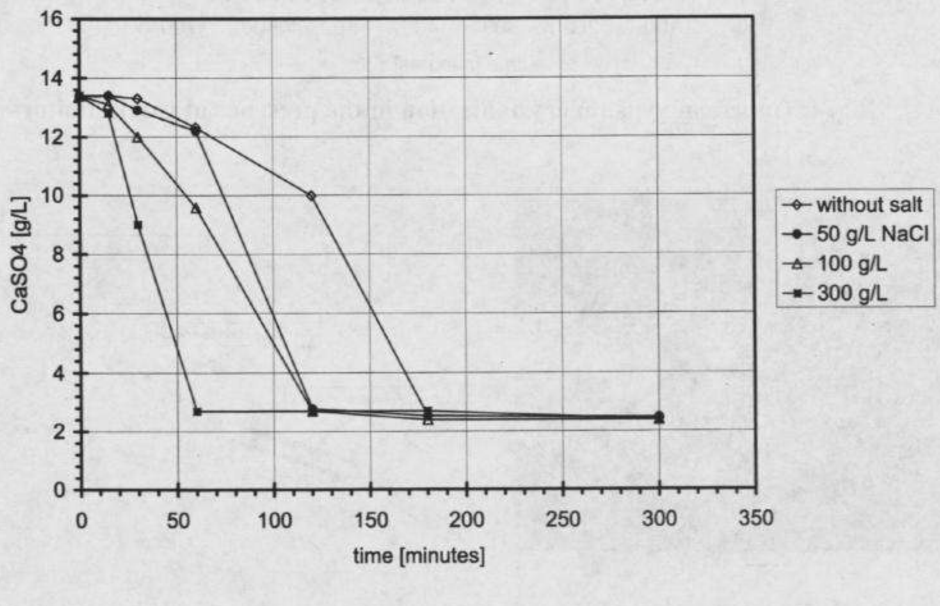


Fig. 2: Stability of supersaturated solutions depending on the salt content at constant inhibitor

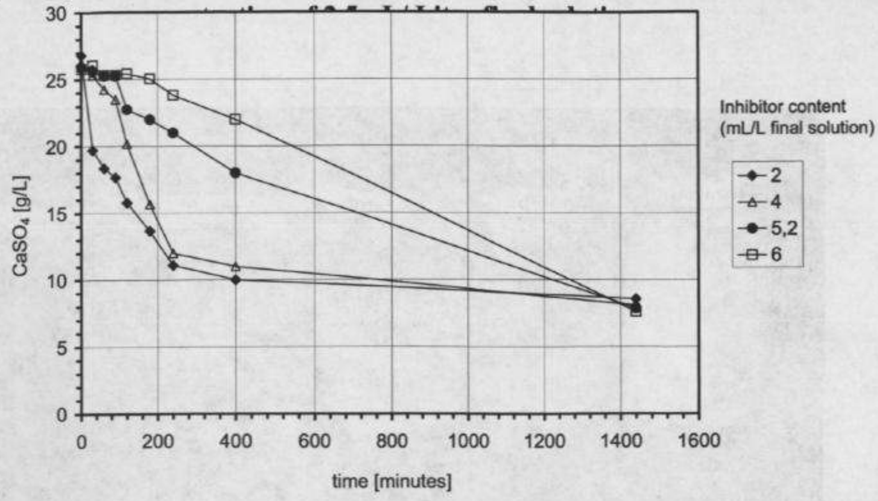


Fig. 3: Course of gypsum precipitation from NaCl-saturated solutions depending on the inhibitor concentration

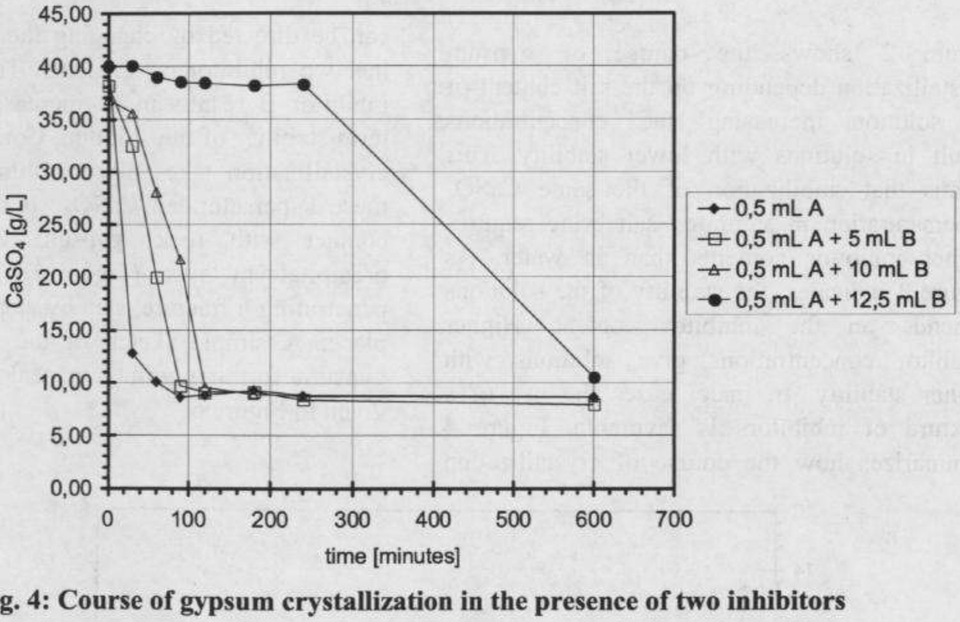
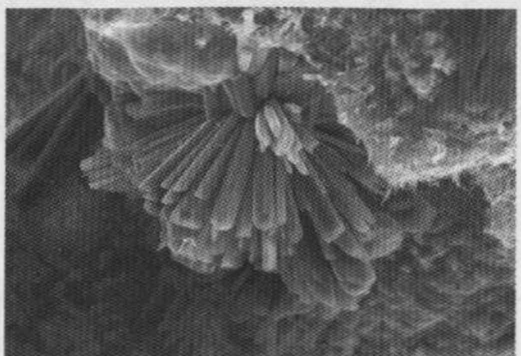


Fig. 4: Course of gypsum crystallization in the presence of two inhibitors



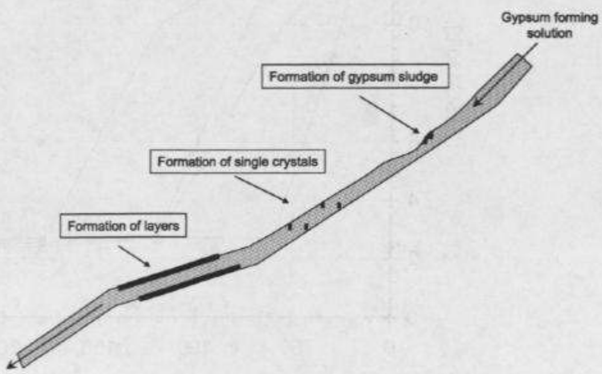


Fig. 5: Gypsum crystals grown from supersaturated solutions

Fig. 6: Action of $CaSO_4$ supersaturated solutions during the flow through fractures

Apart from composition and concentration of the inhibitor the following factors affect the stability of supersaturated solutions:

- temperature,
- flow conditions (turbulent or laminar),
- characteristics of the surface of surrounding rock,
- presence of further components,
- presence of seed crystals and
- chemical stability of the inhibitor.

NaCl saturated solutions containing between 20 and 60 g/L dissolved $CaSO_4$ can be prepared. In the case of complete crystallization, the formation of 19 to 70 kg gypsum per m^3 of injected grout solution is possible. Grouting solutions with short and long term stability can be obtained. These grouting solutions are called **T**ime **R**eleased **G**rout (TRG).

4. Field tests

4.1 Solution preparation

A grout plant was constructed capable of producing up to 200L/min for injection into the Dawson Bay Formation. In all tests original inflow brine or reclaim brine from potash production was used as the main component of the supersaturated solutions. Thus, all solutions were saturated in NaCl avoiding any salt dissolution issues. The grout plant consists of two lines: one line for the preparation of $CaCl_2$-NaCl solution and a second for the preparation of $MgSO_4$-NaCl solution. Stock solutions of $CaCl_2$ and $MgSO_4$ were prepared by dissolution of solid $CaCl_2*2H_2O$ and $MgSO_4*7H_2O$ in fresh water by using colloidal mixers. The resulting highly concentrated solutions were mixed with the salt brine in static mixers. Frequency directed rotary pumps served for pumping of all solutions. The inhibitor was added as a diluted solution to the $CaCl_2$-NaCl brine. The resulting sulfate and calcium solutions were stored in separate tanks until injection. Depending on the required stability of the grout, the final solution was obtained by mixing of both components in the grout plant or at the bottom of the injection well.

Mixing of both solutions in the plant occurred when solutions with extremely high stability were injected. Mixing at the bottom of the injection well requires the installation of tubing in the injection well. One solution was then injected down the annulus and the other down the tubing. The two solutions would then mix at the bottom of the well just before entering the formation. This allows the injection of grout solutions that react quickly while reducing the possibility of the grout reacting in the injection well and/or prematurely grouting the formation. Downhole mixing was used mainly for grouting flow paths with short connection times to the point of injection.

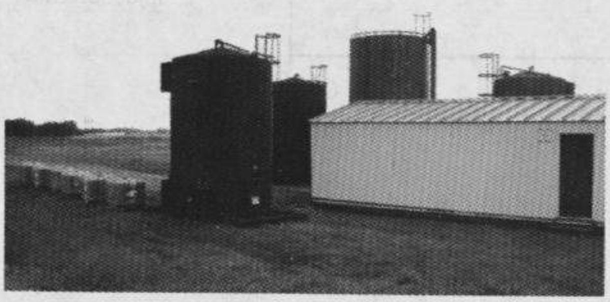


Fig. 7: View of the grout plant with storage tanks for the stock solutions

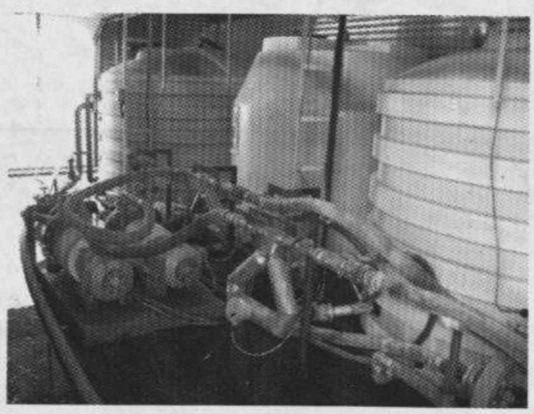


Fig. 8: View into the grout plant

4.2 Hydraulic Properties Changes in Response to TRG

In September 2002 a grout test was carried out with a solution containing an average $CaSO_4$ content of 25 g/L. The injection into well A1 was conducted over a period of 5 weeks. A total of 1280 m³ was injected into the Dawson Bay formation leading to the crystallization of approximately 32 tons of gypsum. During the test inflow rates, inflow chemistry and the pressure in the surrounding injection and observation wells were monitored.

Figure 9 shows the course of the injection pressure and the injection rate. The continuous pressure increase as well as its fluctuations indicates interactions between the grout and the surrounding rock. The maximum possible injection pressure was 1050 psi. After reaching that, the injection rate was reduced. The possibility of injecting for five weeks indicates that the well itself was not prematurely blocked.

Although there were no indications that the grout connected to any inflows, a significant change in the pressure behavior of surrounding wells was measured. Wells situated near the injection well showed an increase in pressure, indicating the sealing of flow paths (Fig. 10). The pumping tests in surrounding wells indicated that there was a significant reduction of the hydraulic diffusivities. This supports the formation of large amounts of gypsum in the treated formation.

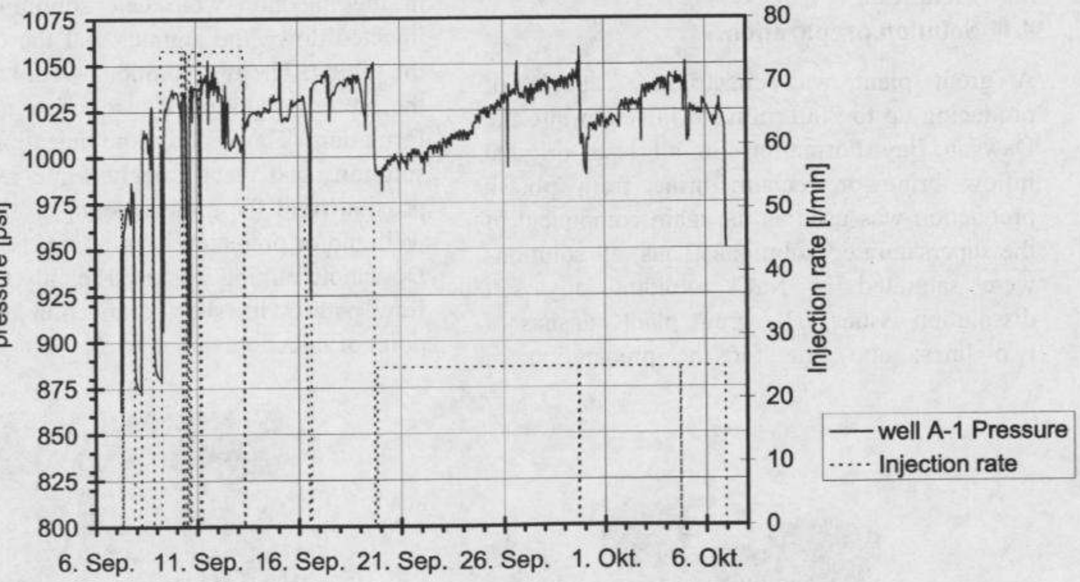


Fig. 9: Injection pressure and injection rate during grouting with long time stable solutions into well A-1

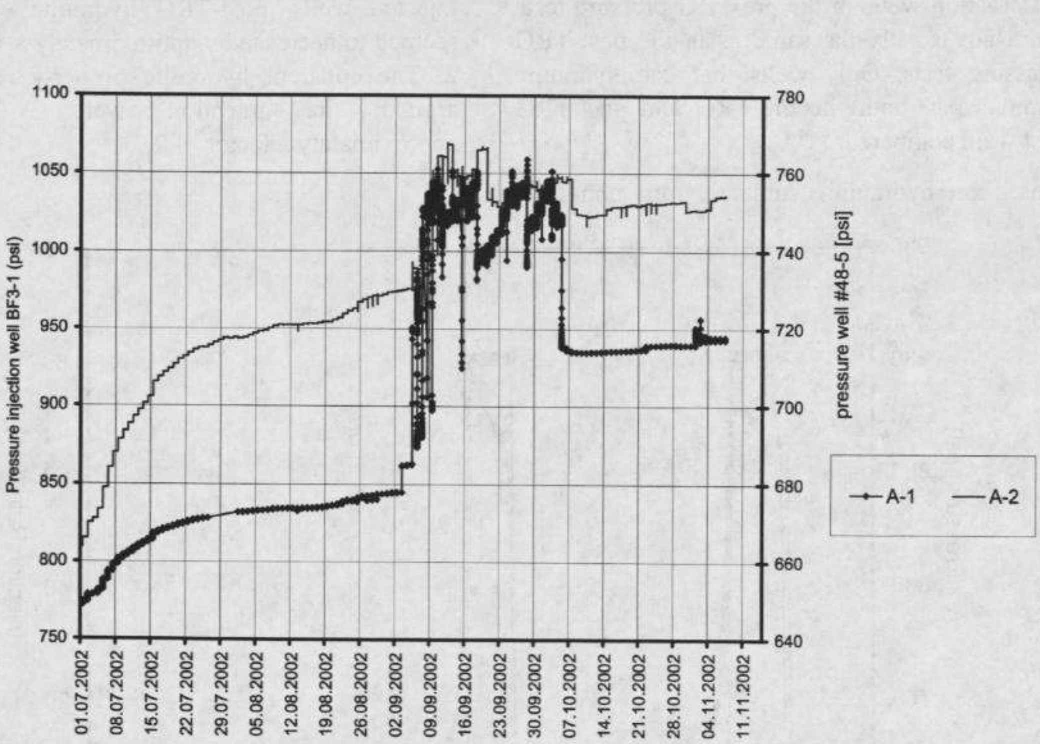


Fig. 10: Injection pressure in well A-1 and resulting pressure increase in the surrounding well A-2

In a second long term test TRG was injected into well A-2 from August 14, 2003 to September 30, 2003. The calcium and sulfate bearing solutions were mixed on the surface during this injection. A total of 3378 m³ grout were injected resulting in approximately 85 tons of gypsum precipitating in the formation. Prior to this TRG field test, hydraulic tests were conducted in the "A" area from April to June 2003.

These tests are herein referred to as pre-TRG hydraulic tests. Post-TRG hydraulic tests were conducted in December 2003. The purpose of the hydraulic tests was to assess the effectiveness of the TRG in reducing the permeability of the formation.

Hydraulic testing consisted of brine injection into a selected well at a constant rate while pressures are monitored in as many other surrounding wells as possible. Figure 11 is an example of the well A-2`s pressure response to the injection rate. The key measurement in the test is the time elapsed between the injection start and the arrival of the induced pressure pulses at the various monitoring wells as shown in Figure 12. Other measurements include the pressure rise in the injection well at constant rates, the pressure decay characteristics in the well when injection stops, the pressure bleed-down characteristics in the injection well when injection stops, and the pressure pulse characteristics in the observation wells. Each pressure test consisted of two short-term injections that lasted approximately 4 hours each. The key measurement data, as described above, were collected in order to estimate hydraulic properties.

The hydraulic properties were estimated using the Hantush-Jacob method. If the data quality was not of sufficient, the approximate Theis method was utilized which was a derived solution based on the classical Theis method. Pre-TRG and post-TRG hydraulic estimates were compared to assess the changes in hydraulic property. In some cases, the set of observation wells in the pre-TRG pressure tests were not exactly the same as in the post-TRG pressure tests. Only wells that had hydraulic estimates in both the pre-TRG and post-TRG test were compared.

Based on hydraulic estimates from non-TRG injected wells, post-TRG hydraulic estimates seemed to decrease by approximately a factor of 2. The apparent hydraulic property reduction around the injection well A-2 was approximately a factor of 7.

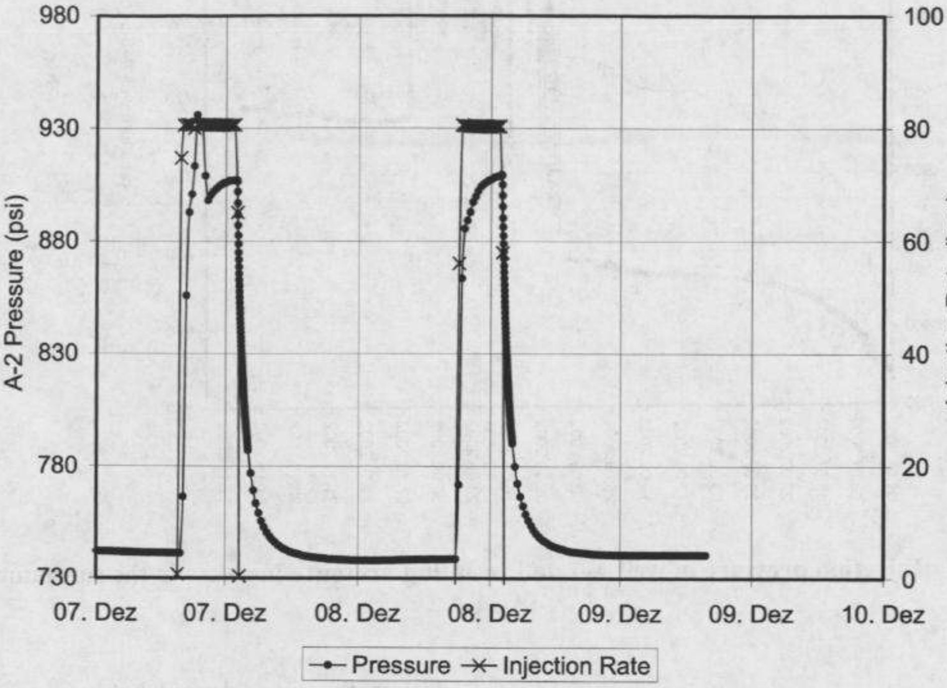


Fig. 11: Course of the injection test in well A-2

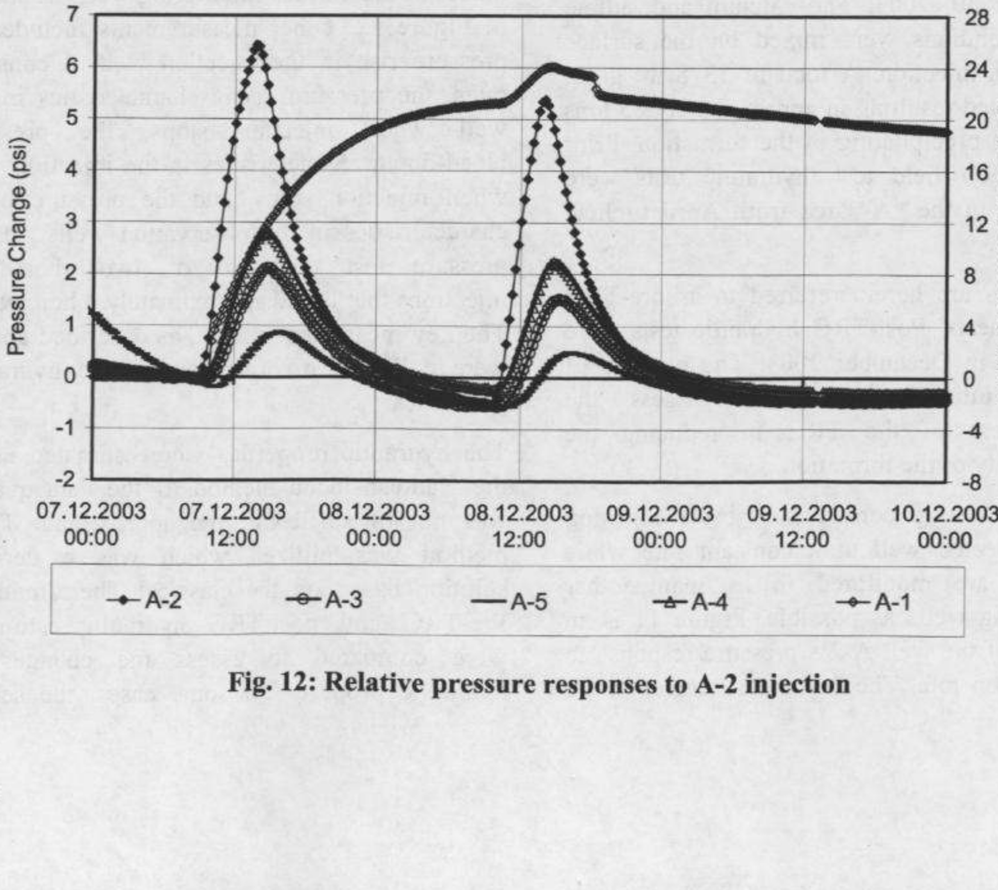


Fig. 12: Relative pressure responses to A-2 injection

4.3 Inflow sealing

During July 2006, a TRG test was conduced in wells E-1 and E-2. The test started on July 12, 2006 and different TRG formulations were used through the injection period. These wells targeted mine inflows that based on tracer test were chemically connected to the injection welis and had relatively short connection times from the top of the well to the inflow.

Based on the short connection times, the decision was made to prepare the grout by mixing at the bottom of the well. In order to prevent the precipitation of the grout in the injection well and / or premature precipitation in the formation, the injections were started with solutions having high inhibitor content. During the test period, the inflow chemistry was continuously monitored. Once elevated calcium and sulphate concentrations were observed in the inflows, the inhibitor concentration was gradually reduced. This decreased the stability of the grout and caused more gypsum to precipitate in the formation.

The composition and the rate of inflow #11 is shown in Figure 13. Increasing amounts of sulfate indicate the replacement of original inflow brine by TRG. Because magnesium sulfate was used as the sulfate source, the magnesium concentrations can serve as an indicator of the amount of TRG reporting to the inflow. On July 17th, the amount of inhibitor in the grout was gradually reduced. While the magnesium concentrations remained stable, as it was expected, decreasing sulfate concentration indicate the formation of gypsum. During the same time period the total inflow rate decreased from 105 gpm to approximately 70 gpm. Similar results were obtained for inflow #12 (Figure 14).

The chemistries of the inflows indicated that approximately 80% of the total TRG injected was reporting into the mine. Due to the use of solutions with high inhibitor contents and thus high stability during the initial period, only 11% reacted and formed gypsum in the Dawson Bay formation. Total inflow in this area started decreasing 5 to 7 days after starting TRG injection and continued through the duration of the test. At the conclusion of this injection, the inflow rate in this area was down 60 to 80 gpm.

This was supported by the Dawson Bay pressure responses. A reduction in inflow rate will result in a pressure increase because the aquifer is recovering to a new higher pressure equilibrium. Prior to the test, the Dawson Bay pressures had a slightly negative trend of -0.42 psi/day and the flow reduction resulted in a new less steep trend of -0.27 psi/day.

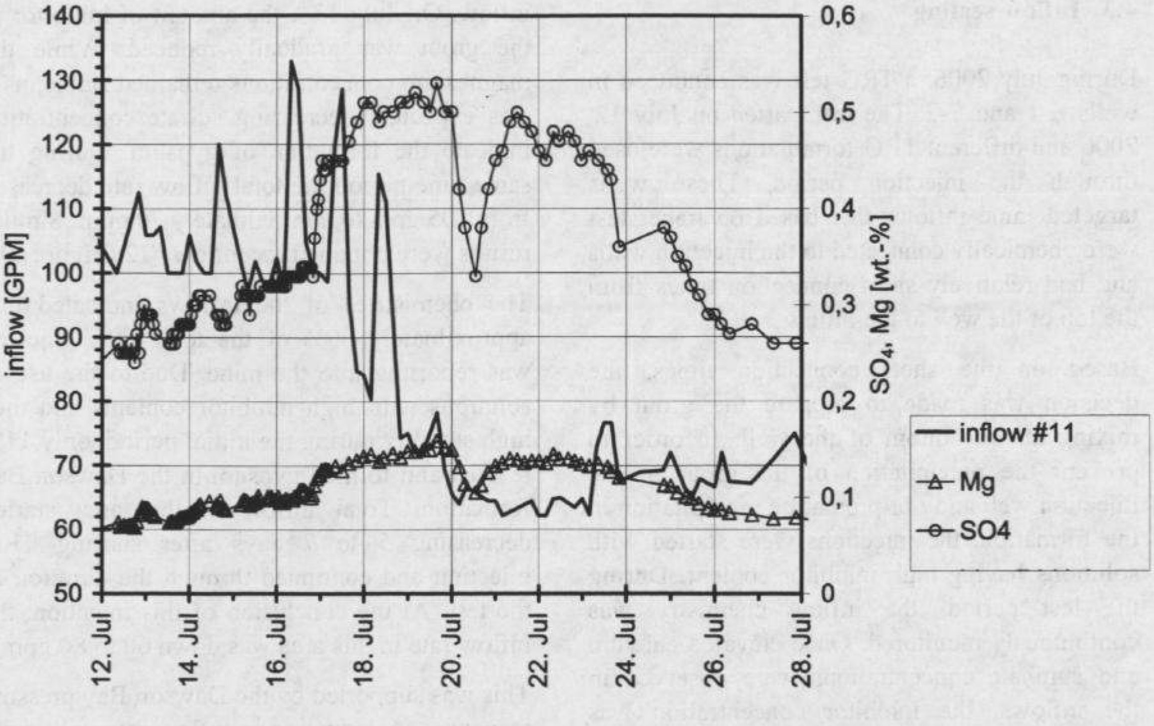


Fig. 13: Chemistry and rate of inflow #11 during TRG injection

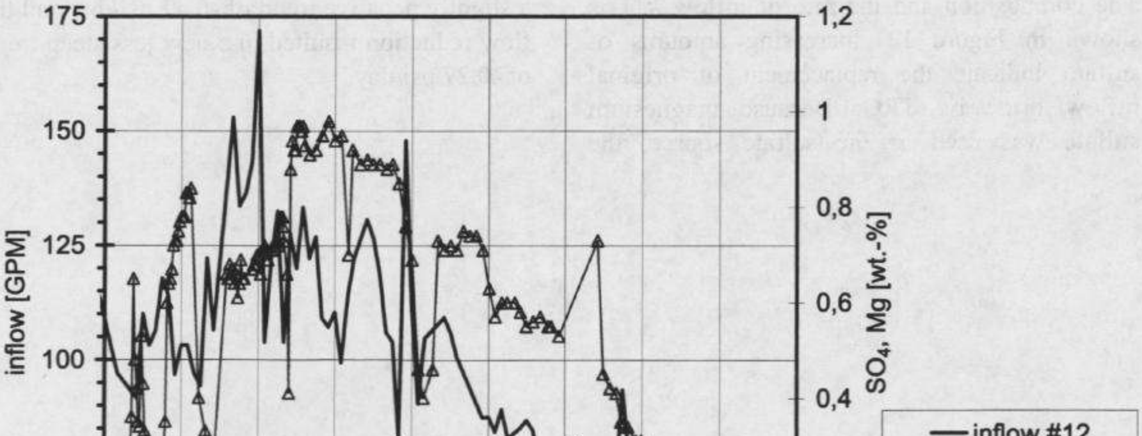


Fig. 14: Chemistry and rate of inflow #12 during TRG injection

5. Summary

Field testing with a supersaturated calcium sulfate solution has shown that sealing of brine inflows is possible by gypsum crystallization. Supersaturated solutions are prepared by mixing $CaCl_2$ and $MgSO_4$ solutions in the presence of suitable precipitation inhibitors. The inhibitors prevent spontaneous gypsum crystallization during the mixing process and give the solutions temporary stability. Gypsum ($CaSO_4 * 2H_2O$) crystallization can be controlled over a period of few minutes to several hours, depending on the degree of supersaturation and the relative inhibitor content. Mixing with the Dawson Bay brine is not necessary to achieve gypsum precipitation. Large scale testing at Mosaic Potash Esterhazy has shown that supersaturated solutions can be prepared and injected without any difficulty. A grout plant was constructed capable of producing up to 200L/min of grout for injection into the Dawson Bay formation. All solutions were saturated in NaCl avoiding any salt dissolution issues. The grout solutions contained between 20 and 60 g/L dissolved $CaSO_4$ resulting in the formation of 19 to 70 kg gypsum per m^3 of injected grout solution, respectively. Grouts with a lower gypsum concentration are more stable and are used for deep penetration of the formation. Grouts with a higher gypsum concentration are less stable and are used for precipitation of gypsum closer to the point of injection. Inflow reductions, changes in the brine inflow chemistry, and changes of formation hydraulic properties interpreted from pumping tests are evidence as to the success of this grouting technology.

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