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A new generation of polyester resin capsules for enhanced health and safety and improved mechanical performance

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Abstract

Styrene is a key ingredient in polyester resin capsules used for rockbolting. However, in the last decade, the knowledge about styrene safety, health, and environmental impact (especially its effects on humans) has increased. Due to health concerns, use of this product in civil construction projects is banned in Europe. For example, the issue of carcinogenicity and harmful effects on fertility or the unborn child were raised. An additional finding and the broader knowledge started raising safety concerns during production and on the end customer's site.

In this paper, characteristics and performance of a new generation of styrene-free resin capsules are discussed. Among the other relevant mechanical parameters (compressive strength and elastic modulus), stiffness in the comparison with standard polyester resin capsules is also discussed.

Finally, the paper presents field validation tests conducted in underground mines in Finland and Spain. In these tests, the focus was set on resin capsule installation, its repeatability and productivity. New styrene-free capsules have been positively tested on commonly used bolting rigs, for instance, Sandvik automatic resin injection (ARI) system.

The obtained laboratory and field data confirm the high performance of new styrene-free capsules and prove their use in underground mines.

Keywords: *styrene-free, resin capsules, rockbolts, carcinogenicity, styrene alternatives*

1 Introduction

Unsaturated styrene-based polyester resin was introduced from the very beginning of the design of encapsulated resin grout for fixing rockbolts. Despite the passage of more than 70 years since the first use of styrene resin for resin encapsulation, it is still used today. This outcome is mainly due to:

- easy control of the rheology of the components of the capsule.
- easy control of the strength of the cured material.
- favourable cost of such a resin, which is used in many branches of industrial production.

The unsaturated resin is a solution of unsaturated polyester and styrene. Polyester is a high-molecular-weight substance and is not particularly problematic in terms of physical and health hazards. Styrene is a low molecular weight substance and poses both physical and health risks. From the very beginning, attention has been paid to styrene's low flash point and its high vapour pressure. This poses a risk of fire or explosion caused by a mixture of styrene and air (oxygen). A more serious health risk which has been identified more recently is the potential carcinogenicity of styrene and the suspected damage to the unborn child (for example, see Vineis & Zeise 2002; Huff & Infante 2011).

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The styrene-free resin capsule is an idea to develop a new resin system that would eliminate both the physical and health risks generated by styrene but, at the same time, would not degrade the result of rockbolting. Solutions that replace styrene with alternate reactive solvent have been known for a long time; an example being the use of vinyl-toluene instead of styrene. Other ways to reduce risk have been the use of styrene vapour-reducing agents or reducing the concentration of styrene in the resin capsule.

In our work, we propose a consistent solution that reduces both physical and health risks. Furthermore, the proposed solution does not worsen, but improves, rockbolting results (for tested rock reinforcement elements). This was made possible using a new styrene-free resin system and its stabilisation method.

2 Styrene: harmful effects of human health

Styrene (CAS no. 100-42-5) is a reactive solvent present in resin capsule composition. The average concentration in the ready resin capsule varies between 7–10%. It is a highly volatile compound (vapour pressure 6.67 hPa at 20°C) with a relatively low flash point (31°C at 1,013 hPa). Styrene is still used in rockbolting products for the mining sector but is already banned for civil construction works (for example, see European Union 2014).

2.1 European Chemicals Agency

According to the harmonised classification and labelling (ATP06) approved by the European Union, this ‘substance causes damage to organs through prolonged or repeated exposure, is a flammable liquid and vapour, causes serious eye irritation, is harmful if inhaled, is suspected of damaging the unborn child and causes skin irritation’ (European Chemical Agency 2023).

Additionally, the classification provided by companies to European Chemicals Agency (ECHA) in REACH (Registration, Evaluation and Authorisation of Chemicals - European Union regulation) registrations identifies that this substance may be fatal if swallowed and enters airways, is suspected of damaging fertility or the unborn child, is harmful to aquatic life with long lasting effects, and may cause respiratory irritation (Table 1).

Table 1 Styrene hazards (European Chemicals Agency)

Hazard class and category code/s	Hazard statement code/s	Hazard statement
Flam. Liq. 3	H226	Flammable liquid and vapour
Skin Irrit. 2	H315	Causes skin irritation
Eye Irrit. 2	H319	Causes serious eye irritation
Acute Tox. 4	H332	Harmful if inhaled
STOT RE 1	H372 (hearing organs)	Causes damage to organs through prolonged or repeated exposure (hearing organs)
Repr. 2	H361d	Suspected of damaging fertility. Suspected of damaging the unborn child

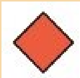
2.2 Occupational Safety and Health Administration

Hazard description:

> *‘Health effects of styrene include irritation of the skin, eyes, and the upper respiratory tract. Acute exposure may also result in gastrointestinal effects. Chronic exposure affects the central nervous system showing symptoms such as depression, headache, fatigue, weakness, and may cause minor effects on kidney function. The following references aid in recognising occupational hazards and health effects associated with styrene.’* (US Department of Labor n.d)

Additionally, *Report on Carcinogens* by National Toxicology Program (2021) identifies styrene as reasonably anticipated to be a humans carcinogen (Table 2).

Table 2 Styrene hazards (Occupational Safety and Health Administration)

Diamond	Hazard		Value	Description
		Health	2	Can cause temporary incapacitation or residual injury.
		Flammability	3	Can be ignited under almost all ambient temperature conditions.
		Instability	2	Readily undergoes violent chemical changes at elevated temperatures and pressures.

3 Determination of laboratory mechanical properties and trial of a new type of styrene-free resin cartridges in underground workings

Research work towards the elimination of styrene from the formulation of resin cartridges progressed in two ways. One was related strictly to the chemical compounds in the resin but the other dealt with the mechanical behaviour of the whole resin cartridge. The aim of the latter was to improve the performance of the resin capsules (i.e. its rigidity and tightness).

Modifications to the foil and end clippings resulted in higher mechanical stiffness of the capsules and reduced product leakages from the capsules, even in adverse conditions (for example, long storage time in a vertical position).

The elimination of styrene as one of the components to produce resin cartridges must not, of course, result in a deterioration of the mechanical encapsulation properties of the new type of capsules for its primary purpose, rockbolting.

3.1 Lab tests of a new styrene-free resin

Typically, resin cartridges are generally produced in two ways, with most manufactured to meet the requirements of local industry standards. However, in some countries, there is a demand that resin cartridges meet the requirements of British Standards Institution (BSI) (2007). These were the requirements for strata reinforcement support system components that were used in British coal mines. In general, the requirements of this standard for resin cartridges are more stringent than those that meet local industry standards.

Examples of resin characteristics in uniaxial compression for a basic version of styrene resin cartridges are presented in Figure 1, and typical normal stress–vertical strain curves for styrene resin cartridges meeting BSI (2007) are given in Figure 2. At 2% strain, there is an ~ 25 MPa increase in uniaxial compressive strength (UCS) observed between the sample sets.

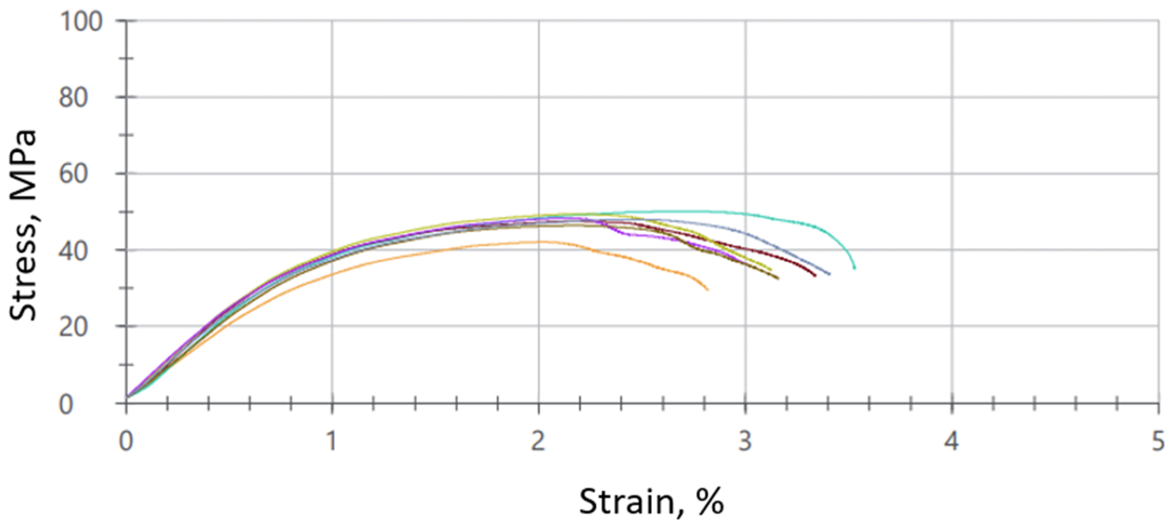


Figure 1 Characteristics of normal stress–vertical strain in uniaxial compression of standard styrene resin cartridges

In general, the UCS of standard formulation styrene resin cartridges is about 50 MPa. For the batch presented in Figure 1, the mean value of UCS is equal to 47.4 MPa (standard deviation 2.63 MPa and coefficient of variation 5.5%). The results (shape of the curves) of all the tested specimens are quite similar and ductility (vertical strain at maximum stress) is about 2.3%.

Mean UCS value for styrene resin cartridges complying with the requirements of the BS standard is equal to 81.7 MPa and again all the results of the individual tests are similar (UCS standard deviation 1.84 MPa and coefficient of variation 2.25%) and ductility is around 2.7%. High compressive strength (in excess of 60 MPa is observed at 1% strain).

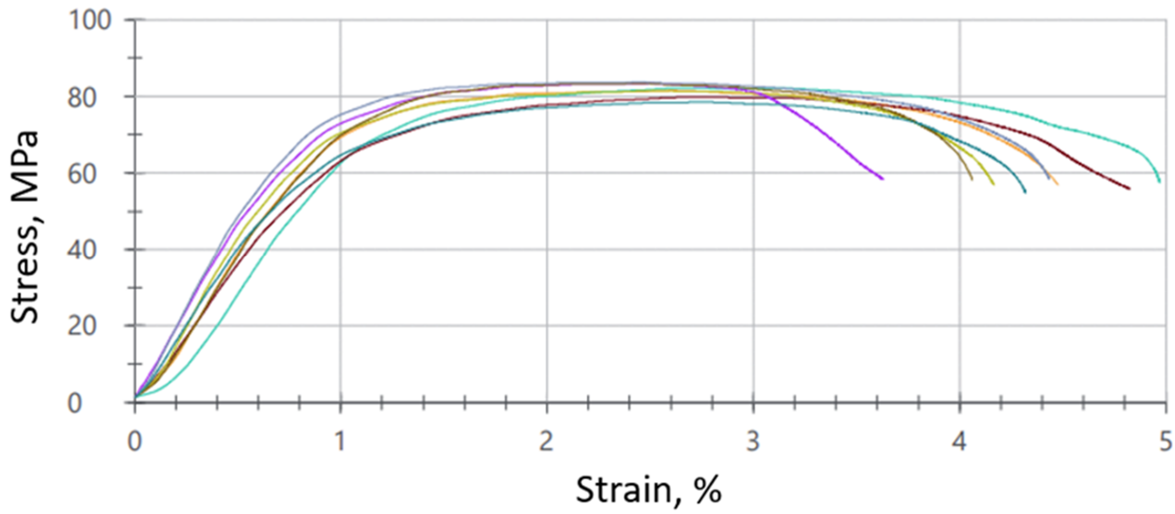


Figure 2 Characteristics of normal stress versus vertical strain in uniaxial compression of styrene resin cartridges complying with the requirements of the BSI (2007)

New formulation of styrene-free resin cartridges results in significantly higher UCS values. The mean UCS value of the tests results presented in Figure 3 is equal to 103.0 MPa (standard deviation 2.08 MPa) and the resin is stiffer (ductility 1.7%). However, there is an increase in covariance seen in the samples at 1% strain and typically, these formulations reduced system ductility.

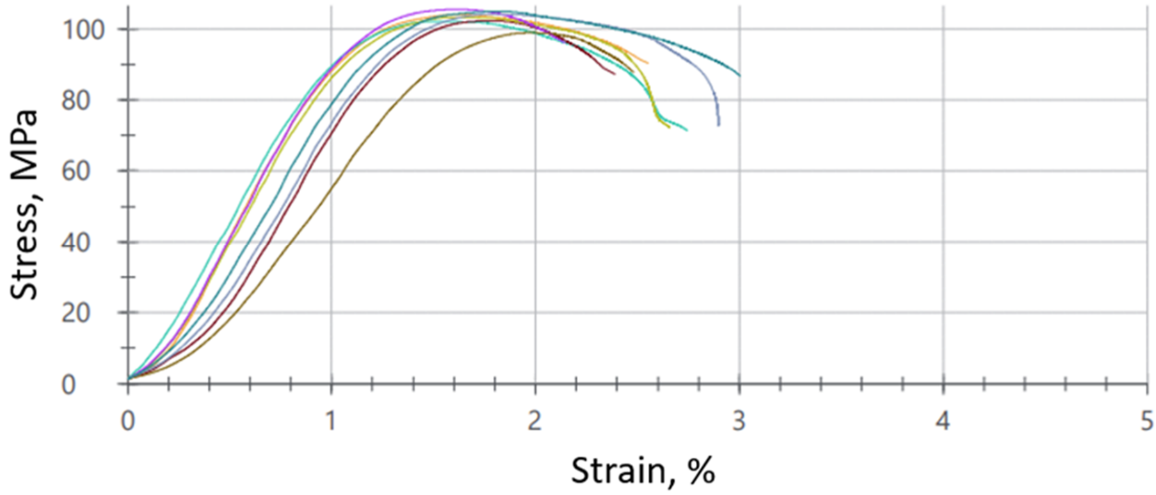


Figure 3 Characteristics of normal stress versus vertical strain in uniaxial compression of a new type of styrene-free resin cartridges

UCS of a new styrene-free resin formulation is at least two times higher than standard styrene-based resin cartridges formulation and about 20% higher than premium version of styrene resin cartridges which comply with BSI (2007).

UCS is not the only mechanical parameter which is important to describe the properties and behaviour of the resin cartridges. BSI (2007) requires the determination of elastic modulus and creep of resin. Elastic modulus is determined, according to BSI (2007), in a procedure of loading and unloading cycles between the 2.5 and 7.5 kN load and the elastic modulus is the mean of the three-secant moduli measured between the two levels of the applied load.

Characteristics of force versus vertical strain in uniaxial compression of styrene resin cartridges meeting the requirements of BSI (2007) are shown in Figure 4. The corresponding curves in the same procedure but for a new type of styrene-free resin cartridges are shown in Figure 5.

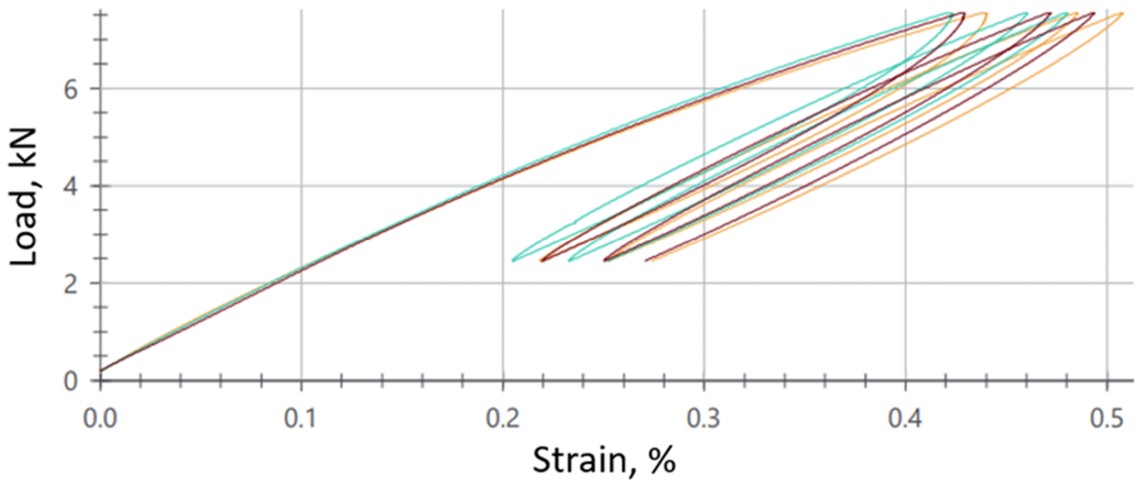


Figure 4 Characteristics of load versus. strain in uniaxial compression of styrene resin cartridges meeting the requirements of the BSI (2007) obtained in the procedure for determining of elastic modulus

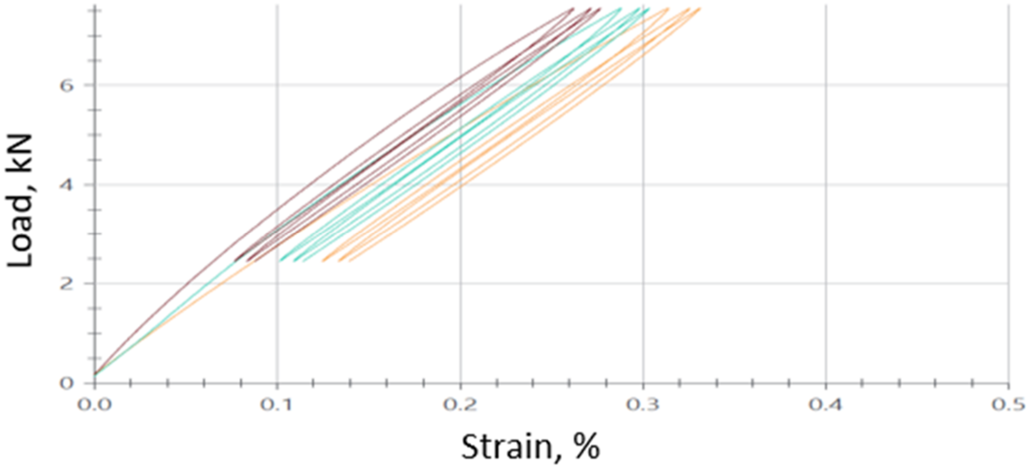


Figure 5 Characteristics of load versus. strain in uniaxial compression of a new type of styrene-free resin cartridges obtained in the procedure for determining of elastic modulus described in BSI (2007)

According to BSI (2007), the elastic modulus shall be greater than 11 GPa. The mean value of the premium version of styrene-based resin cartridges presented in Figure 4 is 14.8 GPa (standard deviation 0.29 GPa and coefficient of variation 1.93%).

A new type of styrene-free resin cartridges is stiffer, with E mean value equal to 17.4 GPa and the scatter of the results is reduced with a standard deviation value of 0.31 GPa and coefficient of variation of 1.78%.

Rigidity of the resin is of high importance in rockbolting, with E value of a range of about 17 GPa which is similar to Young's modulus values of many sedimentary rocks like sandstones or mudstones and more than Young's modulus' values of coal and majority of shales and means that even significant loads exerted on the bolt will result in small deformation (displacement) of the bolt shank.

Rheological properties of the resin cartridges are determined, according to BSI (2007), in a procedure of loading the specimens to a load of 5 kN and maintaining this load for a duration of 15 min. The resistance to creep is the recorded strain between 0.5 and 15 min expressed as a percentage and it shall be no greater than 0.12%.

Example characteristics for creep determination of styrene resin cartridges and for non-styrene resin cartridges are shown in Figures 6 and 7, respectively.

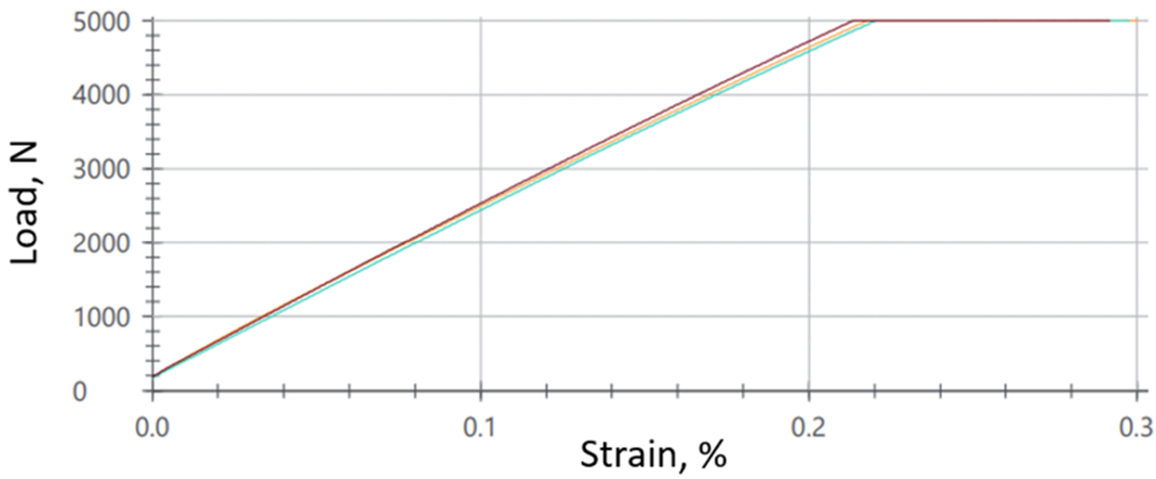


Figure 6 Characteristics of load versus strain in uniaxial compression of styrene resin cartridges meeting the requirements of the BSI (2007) obtained in the procedure for determining of creep

The mean value of the premium version of styrene-based resin cartridges presented in Figure 6 is 0.063% (standard deviation 0.002% and coefficient of variation 3.83%).

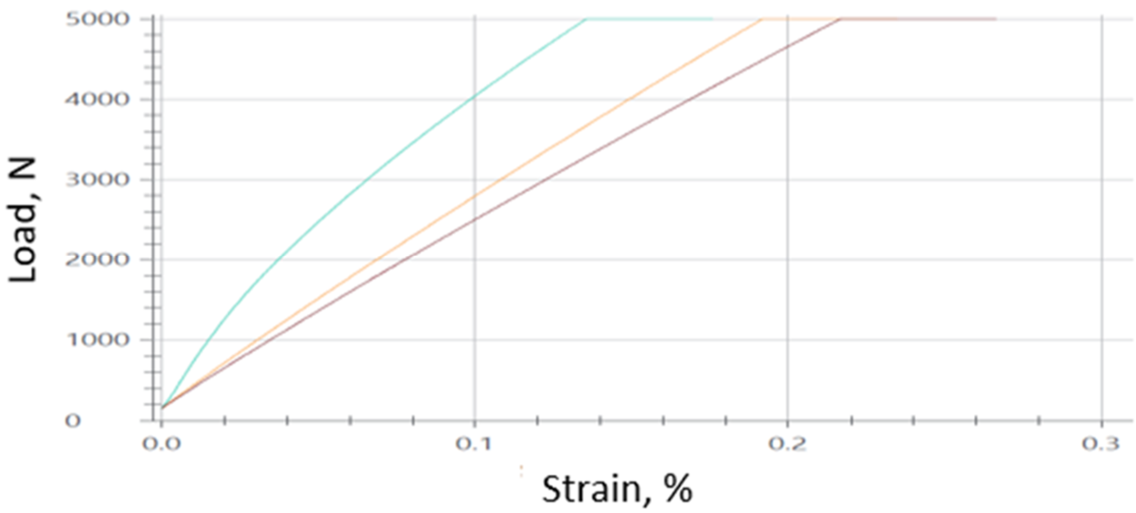


Figure 7 Characteristics of load versus. strain in uniaxial compression of a new type of styrene-free resin cartridges obtained in the procedure for determining of creep described in BSI (2007)

A new type of styrene-free resin cartridges has improved creep resistance with a mean creep value of 0.034%. This is almost two times lower than the creep value for styrene-based resins and is more than three times lower than the required (normative) value given in BSI 2007.

However, the results are not as uniform as in the case of styrene-based resin cartridges and increased scatter of data is observed. It is not known if this is related to the particular batch of the produced styrene-free resin.

3.2 Application trial of a new type of styrene-free resin cartridges in underground workings

Laboratory tests performed confirmed improved mechanical properties of the new styrene-free resin formulation to the existing styrene-based ones. This result, although important, is not sufficient to prove the readiness and usefulness of a new type of resin cartridges (styrene-free) for use in underground workings for rockbolting.

Trials were undertaken to assess the performance of the new resin cartridges (resin, foil and clipping). Numerous short encapsulation pull-out tests (SEPT) were conducted leading to the conclusion of the very good performance of the new styrene-free resin cartridges in those applications.The final test is always the application of the resin cartridges in underground workings in a real mine condition by the crew of the mine using the onsite drilling/bolting equipment and standard rockbolts.

Field trials were undertaken in November 2023, utilising a mechanised Sandvik bolting drill-rig, model DS311 installing DSI Underground 'Atlas 3' rebar bolt grouted with FASLOC SF (styrene-free) resin capsules in a potash mines in Southern Europe.

The most common rockbolts used at the mine are DSI corrugated rebar bolts which are specially designed for the potash mines. These rockbolts feature a forged head, a Ø22 mm corrugated stems made of ductile steel (special grade 'Atlas 3') with ca. 20% elongation. Typically, the rockbolts are 2.4 m long. These bolts are completed by a round plate of Ø150 mm and 6 mm thickness.

The performance of new styrene-free resin capsules was checked using SEPT test procedure, with 300 mm of bolt embedment and 300/900/1500 mm of free end. The SEPT tests were carried out after a one-hour curing period, after installing the bolt, to ensure that the resin has completely cured and gained sufficient strength. After the necessary time has elapsed, an axial load was applied to the end of the bolt and its extension was measured. A view on the rib of the testing gallery before the tests is given in Figure 8 while the equipment assembled to carry out the SEPT tests is displayed in Figure 9.

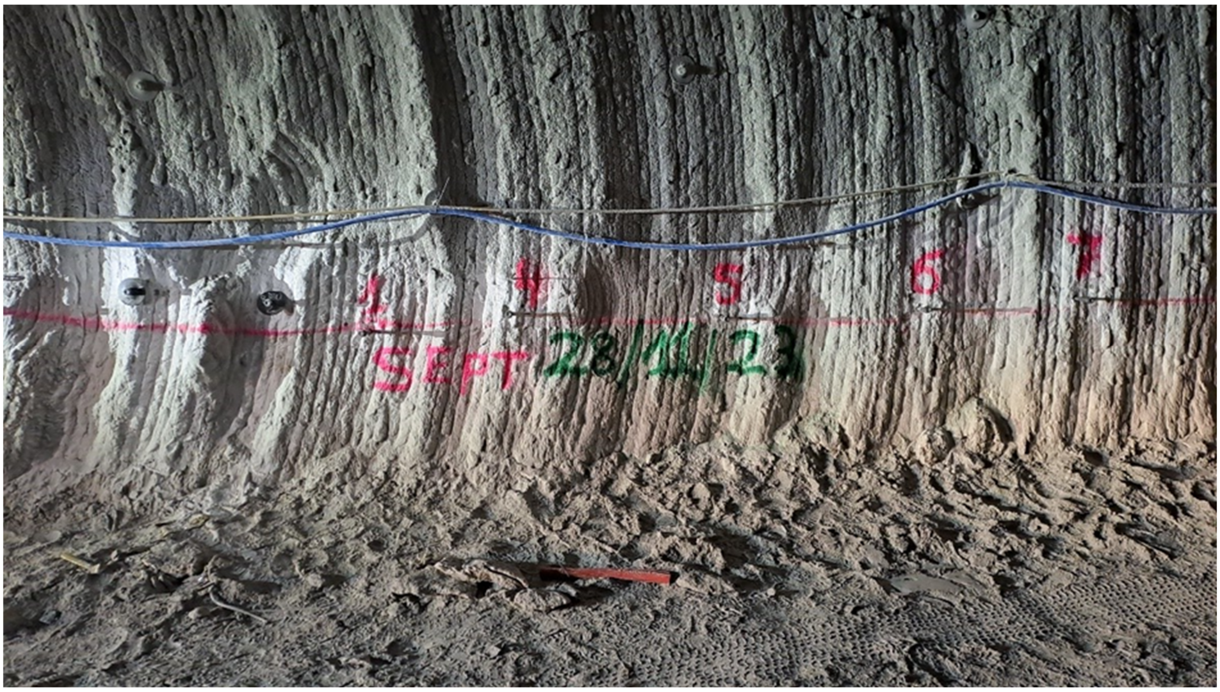
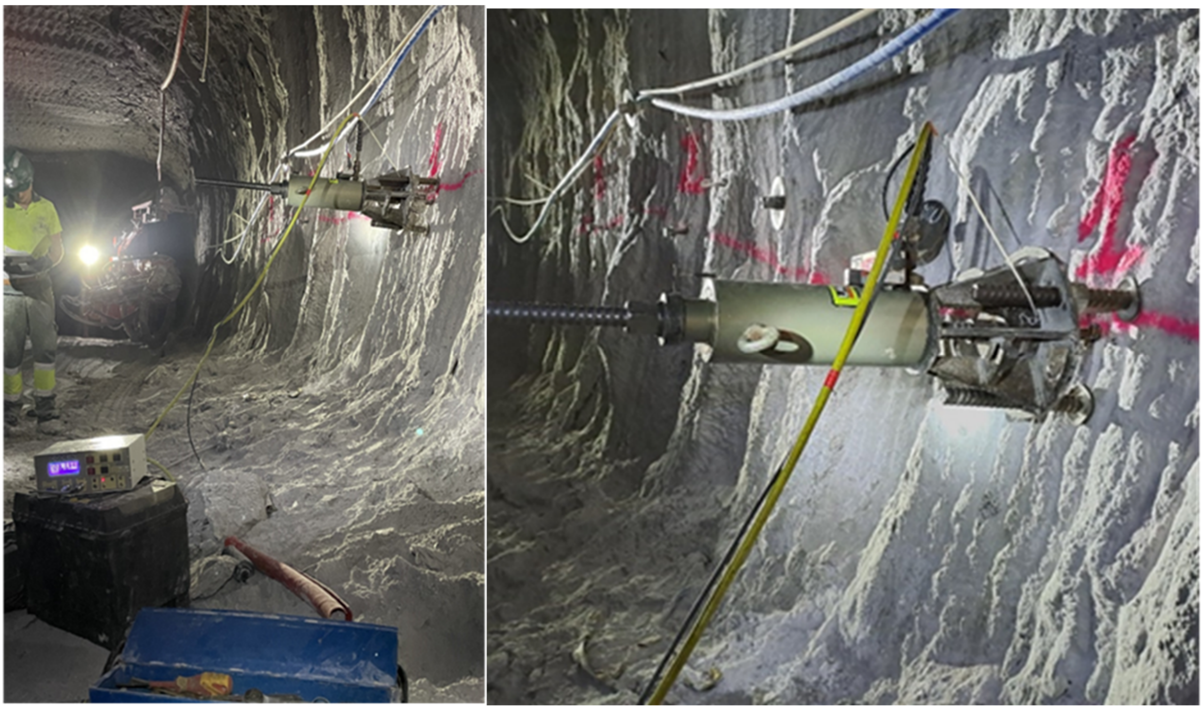


Figure 8 Bolts installed and marked in the rib of the gallery before the tests



(a) (b)

Figure 9 Equipment assembled to carry out the short encapsulation pull-out tests. (a) Broader view; (b) Zoom-in on the pulling out and measuring devices

SEPT tests gave positive results, similar or better than traditional styrene-based polyester resin capsules. SEPT are intended to measure resin's bonding strength on the interface steel-resin and resin-surrounding rock. At the testing site, the surrounding rock is very weak (rock salt) and therefore particularly challenging.

The performance of the new type of resin cartridges was also checked by using FASLOC SF capsules to install roof rockbolts in the testing gallery as well as in the stope area (full rockbolt encapsulation in both cases).

To assess the performance of the new type of resin cartridges in roof bolting, two alternate trials were undertaken. The first trials took place in the same gallery as the SEPT tests where the temperature was about 25°C. Nine standard rockbolts were fully encapsulated in the roof by introducing three FASLOC SF resin capsules into each borehole (Figure 10). Three different gel time formulations of FASLOC SF resin cartridges were tested. Cartridge dimensions were similar (diameter 24 mm and length 600 mm) but the gel time was different (60, 90 and 120 s). There were three rockbolts installed per gel time type of resin. All of the bolts were installed correctly. The most suitable hold time for the temperature and mining conditions at the site was found to be 60 s.

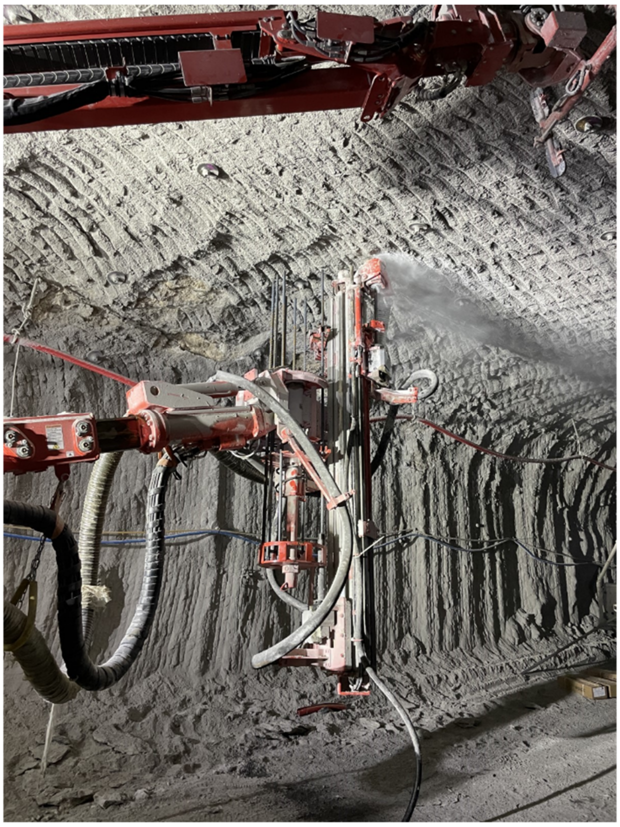


Figure 10 Sandvik DS3111 mechanised bolter drilling in the roof of the gallery. Then shooting FASLOC SF capsules for roof bolting trials (the same gallery as for SEPT tests)

The second trial was carried out in a stope where fresh, unsupported roof was being reinforced and the air temperature was much higher (about 40°C). In two stope areas where two different kinds of bolters operate, the roof rockbolts were installed via the use of new FASLOC SF resin capsules (Figure 11).

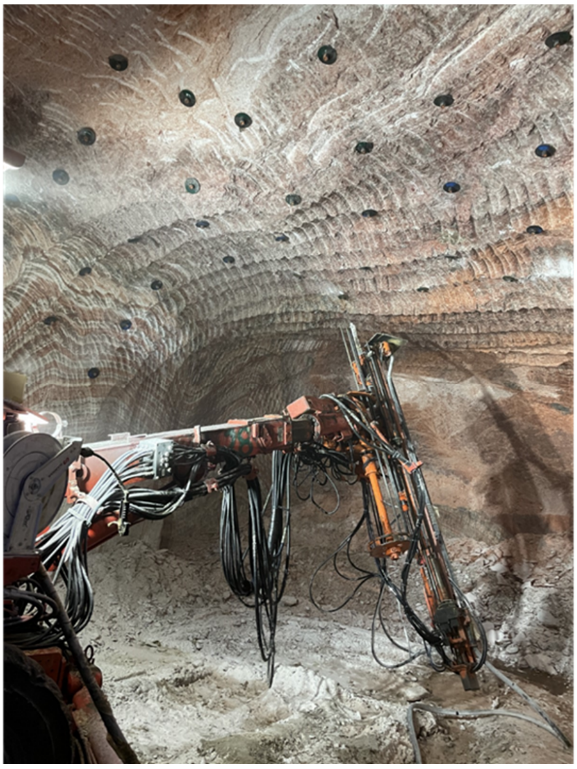


Figure 11 Installation of roof rockbolts with FASLOC SF resin cartridges at the production area

The result was very satisfactory and promising as the validation tests confirm that FASLOC SF, styrene-free resin capsules meet all the requirements set by the mine for its rockbolting and the use of a new type of styrene-free resin cartridges does not change the installation cycle.

A mechanised bolting rig Sandvik DS 311 was used to install the rockbolts. FASLOC SF capsules were injected in the pre-drilled holes using a manual pneumatic launching tube. The manual insertion of the capsule into the launching tube revealed that of FASLOC SF cartridges were very stiff. Capsule stiffness is ideal for mechanised launching systems (such as Sandvik ARI system) and in general is highly appreciated by miners.

4 Conclusion

Styrene-free Fasloc SF represents an important step in reducing chemical hazards in underground roof and sidewall rockbolting application. At the same time, the new formulation delivers improved mechanical load transfer properties and the improved product packaging assures reliable pneumatic installation even when using automatic loading systems such as Sandvik ARI system.

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