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DeepU

DELIVERABLE D1.1

Gas flushing medium for geothermal deep drilling

Report on various liquid and cryptogenic gases suitable for laser-beam drilling

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Disclaimer

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ABBREVIATIONS AND GLOSSARY OF ACRONYMS

Acronym	Extended definition
CA	Consortium Agreement
D	Deliverable
DCM	Dissemination and Communication Manager
D&C	Dissemination and Communication
EC	European Commission
EM	Exploitation Manager
EP	Exploitation Plan
GA	Grant Agreement
HE	Horizon Europe
IPR	Intellectual Property Rights
M	Month
PC	Project Coordinator
PDEC	Plan for Dissemination and Exploitation including Communication activities
SC	Steering Committee
VRE	Virtual Research Environment
WP	Work Package

SUMMARY

Prevent summarized the main characteristics of an appropriate cryogenic gas to be used in laser-beam propulsion drilling. Noble gases such as Argon, Krypton and Helium, as well as Nitrogen, have been considered and compared with regard to their interaction with rocks, sand, aquifers, etc. and with the laser beams. Moreover, they are examined with regard to flammability, explosion risks, environmental sustainability, costs and disposal possibilities.

1. INTRODUCTION

Cold cryogenic gas is to be used in laboratory rock drilling phase with laser-beam propulsion drilling. The gas will be utilized as a shielding gas for the laser head at the bottom of the drill string and after heating-up as a carrier gas for the transport to the surface of the released very small rock cuttings from the bottom of the borehole. The gas is supplied in a supercritical state at low temperatures through newly developed cryogenic pipes, which allow the gas to flow downwards within the load-bearing outer drill string over several thousand meters. The supercritical state of cryogenic gas was chosen for primarily two reasons. The first reason for transferring the gas in a supercritical state is the absence of two-phase flow, which occurs when cryogenic gas is transferred at long distances in a liquid state. In the case of the considered drill string, the temperature difference between the liquefied cryogenic gas and the pipe wall could be significant enough that boiling gas would prevent the flow of cryogenic gas down the pipe. Due to geometry constraints, phase separators would be extremely difficult to be applied, if not impossible at all. The second reason for using the gas in a supercritical state is its high density (comparable to that of a liquid) and relatively high specific heat. It is essential for both of these parameters to be as high as possible, as the cryogenic gas will be conveyed down the borehole inside tubes with an inner diameter of 12 - 18 mm. The high density will help limiting the velocity and pressure drops during flow. The high specific heat will contribute to limiting the temperature increase of the gas due to inevitable heat inflows through the pipes' walls.

The expected temperature conditions in the borehole and the cryogenic pipes and the resulting heat flows, depending on the depth and considered geothermal gradients, still have to be modeled and calculated separately and are not included in this report. These temperature conditions will be included in the following deliverable, dedicated to the drilling test results description. It is assumed that sufficient gas flux arrives in a supercritical state at a sufficiently low temperature at the bottom of the borehole to enable after heating-up a pneumatic transport of the released rock cuttings to the surface.

For an exact forecast of the gas temperature profile and flow conditions, a comprehensive model with all fluid and heat flows must be created, as the thermodynamic and fluid dynamic processes cannot be separated.

This report focuses only on the selection of the most suitable cryogenic gas for the specific laser-beam drilling application planned in the DeepU Project, based on gases specific technical properties and economic evaluations.

2. COMPARISON, ANALYSIS AND SELECTION OF SUITABLE CRYOGENIC GASES TO BE USED IN LASER-BEAM DRILL PIPES

The word cryogenics comes from the Greek words "kruos" meaning "cold" and "genos" - "origin" or "creation", and the concept was proposed by Heike Kamerlingh-Onnes. Currently, the term cryogenics is used to describe methods of obtaining and using temperatures lower than 120 K, specifically 111.1 K, i.e. the boiling point of methane at normal pressure. The boiling point of liquid methane is a conventional limit separating cryogenics from refrigeration established in 1971 by the 13th International Congress on Refrigeration.

The adoption of 120 K as the limiting cryogenic temperature is, of course, arbitrary and results from the historical development of cryogenics, when the main research goal in this field was the liquefaction of gases considered to be stable, i.e. air, oxygen, nitrogen, hydrogen and helium. Note that gases such as propane, butane, chlorine and freons can be liquefied at ambient temperature if they are isothermally exposed to a sufficiently high pressure. This is because the critical temperatures of these gases are higher than the ambient temperature and, through an isothermal increase in pressure, a two-phase state can be achieved, up to complete condensation. In the case of gases whose critical temperatures are lower than the ambient temperature, the increase in pressure alone is not sufficient for these gases to condense. Hence, these gases were called "stable gases" and are now called cryogenic gases. Liquefaction of cryogenic gases is not possible by compressing them without prior cooling.

In almost all industrial and big-scale research applications cryogenic temperatures are achieved thanks to the former liquefaction and evaporation of cryogenic gases. Basic physical properties of cryogenic gases characterised by normal boiling temperature below 120 K are given in Table 1.

Definition of parameters in a phase equilibrium diagram

Critical Point: It is the end point of a phase equilibrium curve. One example is the liquid-vapor critical point, the end point of the pressure-temperature curve that designates conditions under which a liquid and its vapor can coexist. At higher temperatures, the gas cannot be liquefied by pressure alone. At the critical point, defined by a critical temperature T_c and a critical pressure p_c, phase boundaries vanish.

Critical Pressure: It is defined as the pressure above which liquid and gas cannot coexist at any temperature.

Critical Temperature: for a pure substance is the temperature above which the gas cannot become liquid, regardless of the applied pressure.

Triple Point: The temperature and pressure at which the three phases (gas, liquid and solid) of the gas coexist in thermodynamic equilibrium. It is the temperature and pressure at which the sublimation, fusion, and vaporisation curves meet.

Boiling Point: It is the temperature at which the vapor pressure of a liquid equals the pressure surrounding the liquid and the liquid changes into a vapor.

Table 1: Basic properties of cryogenic gases

GAS	M [g]	T_N [K]	ρ_1 [kg/m^3]	ρ_2 [kg/m^3]	ρ_3 [kg/m^3]	T_C [K]	P_C [MPa]	ΔH_V [kJ/kg]	V_2 / V_1 ----	V_3 / V_1 ----
He	4,003	4,2	124,9	16,91	0,178	5,2	0,229	20,3	7,4	701
H_2	2,01	20,3	70,81	1,34	0,089	33,04	1,29	446,0	52,8	788
Ne	20,18	27,17	1207	9,58	0,90	44,5	2,73	85,8	126,0	1341
N_2	28,01	77,3	808	4,62	1,25	126,2	3,39	199,0	175,0	646
O_2	32,00	90,2	1140	4,47	1,43	154,6	5,04	213,0	255,0	797
CH_4	32,00	111,6	423	1,82	0,717	190,5	4,60	510,0	232,0	590

Basic properties of cryogenic gases, M – molecular mass, T_N – normal boiling temperature, ρ_1 – liquid density, ρ_1 – cold vapour density, ρ_1 – gas density at normal conditions, Tc – critical temperature, ρ_C – critical pressure, ΔH_v – latent heat of evaporation, V_1 – liquid volume at 1 bar, V_2 – cold vapour volume at 1 bar, V_3 – gas volume at normal conditions

Generalities on the production of cryogenic gases

The liquefaction of gases on an industrial scale in quantities required for laser-beam propulsion drilling is done predominantly in various modifications of the Claude cycle based on the gas compression, its recuperative precooling and expansion. In case of small demands for liquid gases characteristic for laboratory use, some medical applications and remote locations, the gases can be liquefied with the use of gas cryocoolers and refrigerators based on adiabatic demagnetization of paramagnetic materials.

The atmosphere consists mainly of nitrogen (78 %), oxygen (21 %), argon (0,9%) and small quantities of other gases, including noble ones.

Air separation is done on a large scale by air liquefaction and its later distillation. State-of-art cryogenic air separation plants are characterized by capacities exceeding 3000 tons of O2 from a single technological chain, the separated and liquefied gases are transported in cisterns or supplied by thermally insulated transfer lines. Technical gases may also be delivered to the end user in pressurized cylinders under a typical pressure of 200 bar or transferred in warm gas pipelines. Separation of air with the use of adsorption or membrane technologies is economically justified with the daily capacities not exceeding about 200 tons of obtained gases. Technical gases received from air separation are nitrogen, oxygen and argon. Some air separation units enable the extraction of krypton and xenon, the noble gases whose content in the atmosphere does not exceed several ppm. Helium is cryogenically separated from natural gas, where its content may reach several percent.

Safety considerations on cryogenic gases

Working with cryogenic gases is not without risk. Careless handling of these gases entails considerable risks, such as fire and explosion hazards in the case of oxygen and LNG and asphyxiation in the case of inert gases. There is also a risk of gases losing their liquefied form due to the heat inleaks and consequently creating overpressure in the vessels and other confinements nonequipped with properly scaled safety valves. Examples of known risks in cryogenics are: a) Injury from extreme cold - the cold vapors and gases released from cryogenic liquids can cause injury to the skin. Prolonged contact with cryogenic substances can completely freeze the skin and leave a sensitive skin irritation similar to a severe burn after thawing. b) Fire and explosion risks - a relatively large number of gases are flammable and explode in contact with fire. Flammable gases include hydrogen, methane, liquefied natural gas (LNG) and carbon monoxide. c) Explosion due to rapid expansion - not only fire but also pressure can cause liquid gases to explode in the form of a physical blast. Without sufficiently functioning venting or overpressure relief devices on cryogenic storage containers, enormous pressure can build up in the gases. This can lead to a so-called BLEVE (boiling liquid expanding vapor explosion).

Nitrogen versus Argon as cryogenic gas for laser beam drilling

Based on this general information, we have analyzed 2 gases that could be used for our project; these are Argon and Nitrogen. The most important criterion when selecting the gas for this project is the requirement to find a liquefied gas that remains sufficiently cold over a very long distance, is nonflammable and is available in large quantities at a reasonable price.

Argon is the most common noble gas on Earth, making up around 0.934% of the atmosphere. This makes argon the third most common component of the earth's atmosphere, after nitrogen and oxygen. As argon is produced by the decay of potassium in the earth's crust, it is also found in rocks. When rocks melt in the Earth's mantle, argon, as well as the helium produced by other decays, outgasses. It therefore mainly accumulates in the basalts of the Earth's oceanic crust. Pure argon is extracted exclusively from the air, usually as part of air liquefaction using the Linde process. Other sources for the extraction of argon are air separation for industrial processes including the production of ammonia in the Haber-Bosch process and the production of synthesis gas, for example for methanol production. In these processes, which use air as a starting material, argon and other noble gases accumulate in the production process and can be isolated from the gas mixture. As with the Linde air separation process, the different gases are separated from each other by adsorption or rectification to obtain pure argon. Under normal conditions, argon is a monatomic, colorless and odorless gas that condenses at 87.15 K (-186 °C) and solidifies at 83.8 K (-189.3 °C). As a noble gas, argon hardly reacts with other elements or compounds. Like the other noble gases, argon has no biological significance due to its inertness and is also non-toxic. In higher concentrations, it has a suffocating effect by displacing oxygen. As the cheapest noble gas available in large quantities, argon is used in many areas. Most argon is used as a shielding gas in for instance welding applications. It is always used when the cheaper nitrogen cannot be used.

The following Argon phase diagram shows the phase characteristics with changes in temperature and pressure. The curve between the critical point and the triple point shows the argon boiling points when the pressure changes. It also shows the saturation pressure points when the temperature changes.

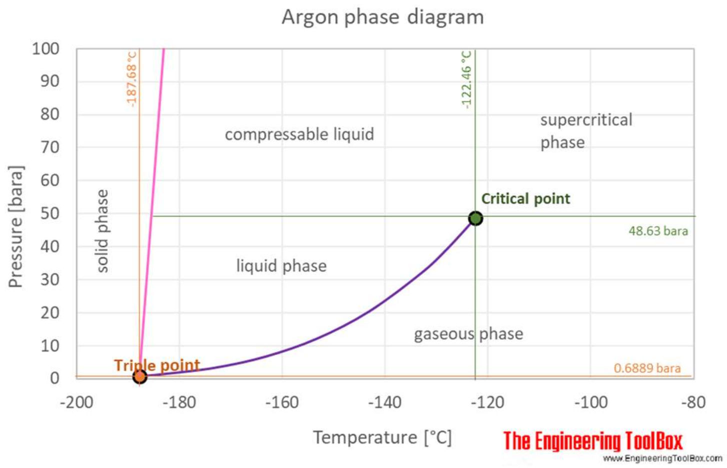

Figure 1: Argon phase diagram (www.engineeringtoolbox.com)

The Earth's atmosphere consists of 78.09 % by volume (75.53 % by weight) of molecular Nitrogen (dinitrogen N2). Today, nitrogen is primarily obtained by fractional distillation of liquefied air in air separation plants using the Linde process with a purity of up to 99.99999 %. Nitrogen with a purity of approx. 99 % is obtained by multi-stage adsorption/desorption on zeolites with capacities much lower than in cryogenic plants. Due to its low boiling point, liquid nitrogen is used as a cooling medium in many applications in industry, medicine and agriculture. Molecular nitrogen is a colorless, odorless and tasteless gas that condenses into a colorless liquid at low temperatures (-196 °C). Although air consists of more than 78 % nitrogen and nitrogen is an inert gas and therefore non-toxic, safety measures must be taken when handling gaseous nitrogen in large quantities, which can cause oxygen deficiency hazard (ODH).

The following Nitrogen phase diagram shows the phase characteristics with changes in temperature and pressure. The curve between the critical point and the triple point shows the nitrogen boiling points when the pressure changes. It also shows the saturation pressure points when the temperature changes.

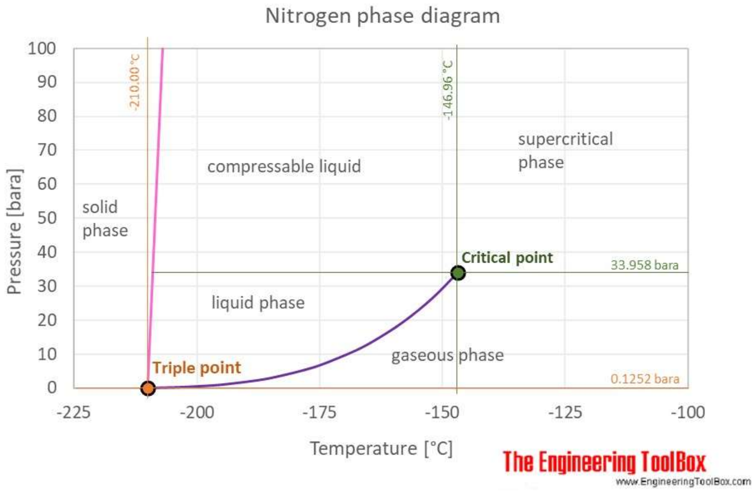

Figure 2: Nitrogen phase diagram (www.engineeringtoolbox.com)

In addition to the design of an optimal lightweight drill string to keep the cryogenic gas in a supercritical state over long distances, we have evaluated the current availability and price levels of various liquid gases. Krypton and Helium are given for comparison.

Table 2: Purchasing prices of Argon, Krypton, Nitrogen, Helium in August 2022 in Germany

Gases	ARGON	KRYPTON	NITROGEN	HELIUM
price free drilling-site Germany delivered in one 20 tons mobile gas tank in August 2022	**2,500 Euro/ton**	not available in August, but similar than ARGON	**400 Euro/ton**	**38,000 Euro/ton**
minimum order	45,000 Euro		6,000 Euro	76,000 Euro
order to be given in advance	6-8 weeks		4-5 weeks	10-12 weeks
price ex factory in August 2022	1,800 Euro/ton		200 Euro/ton	20,000 Euro/ton
providing a 20 tons mobile gas tank on drilling site	10,000€ (one time) 5,000€ (weekly)	10,000€ (one time) 5,000€ (weekly)	10,000€ (one time) 5,000€ (weekly)	not available - Helium is too expensive
liquid gas consumption per 24 hours	30-40,000 liter	30-40,000 liter	30-40,000 liter	
cost of gas per day	approx. 120,000 Euro		approx. 12,000 Euro	
percentage in the atmosphere	0,94%	0,0001%	78%	0%

This table shows the costs and consumption in Germany on a reporting date in August 2022. The prices in the table are subject to strong fluctuations, depending on our purchase volumes, demand from large-scale projects in the surrounding area and availability at the production plants. The absolute prices should therefore also be considered as relative prices. More important for our project is the result that the price difference between the different gases is very high, especially when there is a large daily demand for gas. The price difference between argon and nitrogen is a factor of approx. 10. Based on these economic aspects, only liquid nitrogen should be used for laser-beam drilling.

Thermal insulation solutions in cryogenic systems

Even though nitrogen is the cheapest gas for our application, every effort should be made to keep nitrogen consumption as low as possible, especially as liquid nitrogen consumption is assumed to be up to 100,000 liters per day. To keep the consumption as low as possible, the particular insulation of the cryogenic pipes must be optimized. The thermal insulation of the cryogenic pipes plays a central role in cryogenics. Cryogenic gases must be kept at the perfect temperature so that they can be used in a cold state, which is no easy task. Liquid or supercritical gases are sometimes transported over several kilometers, e.g. from a terminal through various transfer pipes to a refrigeration plant, a ship, a launching platform or another destination, and at each step and during the entire transport route there is a possibility that the gas will heat up and escape. A small heat leak can have a significant impact, therefore making optimal cryogenic insulation is extremely important. In recent years, vacuum technology has proven to be the best technique to maintain the (cryogenic) temperature of transfer pipes. Compared to conventional insulation, the insulation value of vacuum insulation is much higher, which means that there is less heat loss and fewer gases are lost. Compared to insulation made of e.g. PIR/PUR, Foamglas, Armaflex, Perlite and Misselon, vacuum insulation offers an insulation value 15 times higher according to Demaco *(www.demaco.nl)* than any other method.

Vacuum technology refers to the use of a vacuum or high vacuum for optimum insulation of transfer lines or pipes. This involves creating the thinnest possible vacuum ring space between two pipes, which are then double-walled pipes and all the air between these two pipes is extracted. This creates a pressure difference between the vacuum in the ring space between the two pipes and the outside air, which keeps a large proportion of the ambient heat out of the inner pipe system. But why does vacuum insulate pipes so well? Liquid gases are heated in three different ways: a) by Conduction: essentially by heat conduction in direct contact. When two objects come into contact, the heat is generally transferred directly from the warmer to the colder material. This also applies to liquid gases. b) by Convection: this is heat generated by the movement of molecules. The more the molecules are in motion and collide with each other, the more heat is generated. c) by Radiation: radiant heat can be radiation from the sun or any other heat-emitting body like drilled walls and heat from the laser beam.

In cryogenics, the best thermal insulation solution is crucial. While there are a variety of different insulation methods, for our project we are focusing on vacuum pipes or pipes manufactured of low thermal conductivity materials to keep the gas sufficiently cold over a very long distance.

Considerations on the use of Nitrogen in laser beam drilling

Below are the answers to several important questions that came up during the project and are briefly addressed here.

a) How does the process gas interact with the groundwater in the borehole, and can it be dangerous?

The process gas, in our case nitrogen, can dissolve in groundwater in a borehole, especially if the surrounding soil or atmosphere has a high concentration of nitrogen. However, since laser drilling in groundwater is very difficult and the very high temperatures in the borehole bottom displace the groundwater in the soil, we assume that the nitrogen gas does not pose any risk.

b) How does process gas interact with natural gas or crude oil in the borehole and can it be dangerous?

Nitrogen gas can be used in the oil and gas industry to enhance oil recovery by injecting it into reservoirs to maintain pressure and displace oil towards production wells. When nitrogen gas comes into contact with natural gas or crude oil in a borehole, it can help improve the flow of hydrocarbons to the surface. Nitrogen gas can react with crude oil to form nitrogen oxides. This reaction can occur at very high temperatures but is not normally spontaneous or explosive.

c) Is there a process gas effect on the laser glass lenses?

In nominal operational conditions, the cryogenic nitrogen gas has no direct effect on the laser lenses, because there is no temperature shock to the laser lenses, but a steady, cold stream of nitrogen. Nevertheless, the cryo pipes and the proximity of the lense will be cooled from ambient temperatures (at which it will be constructed) to cryogenic temperatures. This will cause the pipes, lense and the lenses mount elements to thermally contract. The thermal contraction of different materials is different which can induce stress in the lenses. This effect needs to be taken into account during the design of the lenses mounting rig.

d) Is there an influence of cold gas on stainless steel pipes?

During cryogenic gas contact with stainless steel, no chemical reactions occur. The low temperature of the gas cools down the stainless steel components. As the temperature decreases, thermal contraction of the stainless steel occurs. This can lead to stresses and deformations in the material. It is important to consider the thermal contraction of stainless steel pipes in the design to avoid any damage.

e) What is the flammability of the process gases?

The risk of flammability of hot nitrogen and argon is extremely low, as the gases are non-flammable. Nitrogen is an inert gas, which means that it cannot react with other substances and is therefore not flammable.

f) Are there any explosion risks in the borehole due to the process gases used?

Nitrogen gas is not flammable, therefore there is no risk of combustion explosion. Nevertheless, the gas in a cryogenic state during the increase of temperature expands. If the outflow of the gas is blocked, the expansion of the gas leads to the pressure increase. Without sufficiently functioning venting or overpressure relief devices on cryogenic storage containers, enormous pressure can build up and lead to the cryogenic expansion explosion.

g) Can process gases damage the environment?

Nitrogen and noble gases are generally inert and have no direct negative impact on the environment if they are used and disposed of correctly. As nitrogen is produced by fractional distillation of liquid air using the Linde process because liquid nitrogen has a lower boiling temperature (-196 °C) than oxygen (-183 °C), no additional gases are released that would contribute to global warming.

h) How can the drilling cuttings and gas blown out of the borehole be collected and disposed of on the surface?

The gas-cutting mixture flowing out of the borehole can be collected via an ejection preventer above the borehole and fed into a cyclone separator, which separates the cuttings from the gaseous nitrogen. The filtered and purified nitrogen gas is pumped into a tank from where it is converted to liquid nitrogen. The cuttings can be analyzed and then used as additives in road construction, for example.

i) Can the gases be produced in large quantities on site, or must there be a plant near the borehole to provide liquid gas?

The estimated maximum nitrogen consumption ranges from about 1 to 4 kilograms per second. This amount requires constant deliveries of liquid nitrogen to cryogenic tanks located near the drilling site. The cryogenic tanks should be equipped with appropriate vaporizers and pumping systems to ensure the required temperature and pressure at the inlet to the drill string. Due to the high costs of building air separation and nitrogen liquefaction units and the impracticality of transporting such air separation and nitrogen liquefaction installations, it seems uneconomical to install them at the drilling site. It is preferable that the stationary air separation plant be located within a maximum radius of 300 km.

j) Can interactions occur between the gases and the laser beams in the inner tube?

The interaction between nitrogen and laser beams can vary depending on the specific conditions and characteristics of the laser beam. Here are some possible interactions: a) Absorption: nitrogen can absorb laser beams, especially in the ultraviolet range. This can cause the nitrogen to heat up and in some cases lead to chemical reactions. b) Diffusion: Laser beams can be diffused by nitrogen molecules, which leads to a distribution of light energy. c) Ionisation: under certain conditions, the interaction between nitrogen and a strong laser beam can lead to the ionisation of nitrogen molecules, resulting in electrically charged particles.

Overall, the exact type of interaction between nitrogen and laser beams depends on various factors, including the wavelength of the laser, the intensity of the beam and the chemical composition of the medium in which the nitrogen is located.

3. REFERENCE LITERATURE

- A. F. Holleman, E. Wiberg, N. Wiberg: Lehrbuch der Anorganischen Chemie. 102. Auflage. Walter de Gruyter, Berlin 2007, ISBN 978-3-11-017770-1, S. 651–743.

- N.N. Greenwood, A. Earnshaw: Chemie der Elemente. 1. Auflage. VCH Verlagsgesellschaft, Weinheim 1988, ISBN 3-527-26169-9, S. 518–607.

- M. Chorowski, Kriogenika podstawy i zastosowania (Cryogenics, basics and applications), MASTA, 2007, ISBN 978-83-921555-3-9.