HOLE FLUIDS FOR DEEP ICE CORE DRILLING: A REVIEW

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Copenhagen
1999

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INTRODUCTION

The contemporary stage of ice core drilling began about 1950. The first experience of deep drilling showed the significant hole closure in an open hole. The deepest “dry” bore-holes were 411 m (Site 2, Greenland, 1957) and 952 m (Vostok Station, Central Antarctica, 1972). For drilling at larger depths it is necessary to prevent the hole closure by filling of the bore-hole with a fluid. Fluids used at rock drilling are not suitable for ice drilling. Only special low-temperature fluids are fit.

For the first time the drilling in ice with fluid was made by USA CRREL at Camp Century in 1966 and then at Byrd Station in 1967 - 1968. The lower part of the bore-holes was filled by the aqueous ethylene glycol solution and the upper part was filled by the mixture of diesel fuel of arctic blend DF-A with the densifier (trichlorethylene).

During thirty years after this event not much deep bore-holes in ice were drilled (*Table 1*). The unfortunate choice of the type and the parameters of the fluid often caused sticking of the drill. Therefore, the choice of the fluid for the concrete drilling conditions is considered to be one of the most important parts of ice drilling technology (*Gundestrup*, 1989).

The main parameters of fluids used for ice deep drilling are:

1) density and fluid top;
2) viscosity;
3) frost-resistance;
4) stability;
5) compatibility with polymers and metals;
6) volatility;
7) flammability;
8) ice and water solubility;
9) toxicological and environmental characteristics;
10) cost.

This review of hole fluids for deep ice core drilling includes the necessary theses, equations, examples and properties data for the optimal choice of the hole fluid for the concrete drilling site.

Table 1. List of the deepest bore-holes in ice

Years	Location	Organization or Project	Depth, m	Fluid	Notes
1966	Camp Century, Greenland	USA CRREL	1391	Aqueous ethylene glycol solution; Fuel DF-A + trichlorethylene	
1967-1968	Byrd Station, Antarctica	USA CRREL	2164	Aqueous ethylene glycol solution; Fuel DF-A + trichlorethylene	The drill was stuck in year during the resumption of the drilling
1972	Novolazarevskaya Station, Antarctica	Arctic and Antarctic Research Institute, USSR	812	Aqueous ethanol solution	The hole was plugged by ice chips
1980-1981	Dye 3, Greenland	University of Copenhagen, GISP	2037	Fuel Jet A-1 + perchlorethylene	The drill was stuck
1980-1986	Vostok Station, Antarctica	Leningrad Mining Institute, USSR	2202	Fuel TS-1 + CFC 11	The drill was stuck
1986-1989	Vostok Station, Antarctica	Leningrad Mining Institute, USSR	2546	Fuel TS-1 + CFC 11	The drill was stuck
1990-1992	Summit, Greenland	University of Copenhagen, GRIP	3029	Solvent D60 + CFC 113	
1990-1993	Summit, Greenland	University of Alaska, GISP2	3053	n-Butyl acetate	The cable was damaged
1991-1993	Law Dome, Antarctica	Australian Antarctic Division	1196	Fuel Jet A-1 + perchlorethylene	
1996-1997	Camp North GRIP, Greenland	University of Copenhagen, NGRIP	1371	Solvent D60 + HCFC 141b	The drill was stuck
1996-1998	Dome F, Antarctica	Japanese Antarctic Research Expedition	2500	n-Butyl acetate	The drill was stuck
1990-1998	Vostok Station, Antarctica	St.Petersburg Mining Institute, Russia	3623	Fuel TS-1 + CFC 11; Fuel TS-1 + HCFC 141b	

1. TYPES OF HOLE FLUIDS FOR DEEP ICE CORE DRILLING

Classification of ice drilling fluids

In practice of deep ice drilling only three types of bore-hole fluids have been used:

1) petroleum oil products (fuels or solvents) containing densifier;
2) aqueous ethylene glycol or ethanol solutions;
3) n-butyl acetate.

Probably, one of the most promising drilling fluids is silicon oil. All foregoing liquids have there own advantages and disadvantages discussed below.

We can propound the additional division of bore-hole fluids for deep ice drilling on the following two criteria: low-temperature properties and ice/water solubility. According to the first criterion drilling fluids are divided into three main groups (*Table 1*):

(a) drilling fluids for cold glaciers with minimal temperatures –60/-50 °C (Central Antarctica);

(b) drilling fluids for cold glaciers with minimal temperatures near –30 °C (Greenland, some parts of Antarctica);

(c) drilling fluids for temperate glaciers with temperatures above –15/-10 °C (arctic ice caps, mountain glaciers).

Table 1. Classification of drilling fluids for deep ice core drilling

Ice/water solubility	**Minimal temperatures of ice, °C**		
	From –60 to -50	**Near -30**	**Above –15/-10**
Hydrophobic liquids	Low-temperature petroleum oil products + densifier	Petroleum oil products + densifier	Petroleum oil products + densifier
	n-Butyl acetate	n-Butyl acetate	n-Butyl acetate + anisole
	-	Silicon oil	Silicon oil
Hydrophilic liquids	-	-	Aqueous ethylene glycol and ethanol solutions

According to ice/water solubility drilling fluids are divided to:

(a) hydrophobic liquids that are stable to water and ice;

(b) hydrophilic liquids that are able to blend with water in any concentration and dissolve ice at negative temperatures.

The main drawback of the use of hydrophilic liquids is the dissolving of ice from bore-hole walls up to equilibrium concentration of the solution. The equilibrium concentration of hydrophilic liquids depends on temperature, and, therefore, the bore-hole temperature changes cause the freezing of water from aqueous solutions and the formation of slush in bore-hole.

Petroleum oil products

The petroleum oil products are extremely complex mixtures of organic compounds (aromatics, naphthenes, olefins, paraffins). They can contain some amounts (not more then 1-2 %) of inorganic components (sulfar, nitrogen, oxygen and trace metals).

Problems with petroleum oil products at extremely low temperatures are largely due to wax formation, increased viscosity, decreased volatility and contamination by water (*Diemand*, 1991). For deep ice drilling the oil products of kerosene type only are suitable, and they are composed chiefly of paraffins and naphthenes. The naphthenes have very low freezing point and, therefore, impart good low-temperature properties to the kerosenes.

Low-temperature fuels DF-A, Jet A1 and JP-8 usually used for ice deep drilling are all kerosenes and virtually indistinguishable, the only difference between them being the nature of the additive package.

Diesel fuel DF-A is arctic-grade diesel fuel and used for high-speed diesels at air temperatures below –30 °C. The main problem associated with the use of DF-A in diesel engines is the result of low viscosity and lubricity, which can cause premature wear of fuel pumps and injector systems. However, this problem is insignificant in cold regions because the fuel viscosity at low temperature increases to the values of standard diesel fuels at normal operating temperatures.

Turbine fuel Jet A1 is one of the main fuels for jet engines. It is used mainly for overseas carriers because it has a lower freezing point by comparison with other turbine fuels (Jet A and JP-5). Jet A1 often relabeled and supplied by fuel distributors as diesel fuel DF-A.

Turbine fuel JP-8 is similar to fuel Jet A1, but it contains a corrosion inhibitor, an anti-icing agent and anti-static compound. The fuel JP-8 is being considered by the US military as a single fuel for all jet and turbine aircraft and diesel engines involved in its combat operations.

Aircraft fuel TS-1 is used in Russia as one of the main jet fuels for airplanes with subsonic speed. The fuel TS-1 has better low-temperature properties than fuels DF-A, Jet A1 and JP-8, and therefore it can be used at lower bore-hole temperatures.

Other kinds of oil products suitable for deep ice drilling are petroleum solvents intended for cleaning and other purposes.

LVT-200 is a refined petroleum hydrocarbon product manufactured by CONOCO Co. (*Gosink et al.*, 1989). The content of aromatics in LVT-200 is lower then in diesel fuel, but its viscosity is too high (near 17 cP at –40 °C), and it is not dense enough for ice core drilling.

Bromoil, or ***permoil***, was projected for use during the first 1990 drilling season at Summit, Greenland (GISP2 Project). Bromoil is a mixture of LVT-200 and polybrominated biphenyl ether (PBBE). This mixture was developed for high temperature well boring and produced by OSCA Co. *Gosink et al.* (1989) didn’t recommend using of bromoil because of its serious disadvantages (high viscosity of about 13 cP at –19 °C and significant human and environmental risk).

Solvents of Exxol D types (Exxol D30, D40 and D60) are kerosenes that are manufactured by Exxon Chemical International. Solvents of Exxol D types are characterized by low aromatics content (less than 0,5 %) and a narrow boiling range than low-temperature fuels (*Gundestrup et al*., 1994a). They are differed by composition of hydrocarbons and therefore by density-viscosity properties.

Solvent IP-1620 has similar components and properties as solvent Exxol D60 (*Fujita et al.*, 1994), ant it is manufactured by Idemitsu Company (Japan), a company, which produced petrochemical products. Solvent IP-1200 can also be used as a fuel oil.

Densifiers

Kerosene type hydrocarbons, mostly used as drilling fluid, have the density of about 800 - 850 kg/m^3 at –30 °C compared to 920 kg/m^3 for ice. Therefore, usually they are made denser by addition of various densifiers of halogenated hydrocarbon or fluorocarbon types. The progress here may be illustrated by scheme at *Fig.1*.

The main disadvantage of the most of densifiers is significant health hazard and environmental risks. The organic densifiers used or suitable for blending with petroleum fuels and solvents are listed in *Table 2*.

Halogenated hydrocarbons are manufactured in a petroleum oil production and are used usually as solvents for fat depriving and extraction, chemical clothes cleaning, and so on.

Fluorocarbons (synonyms: FC, fluorocarbon refrigerants, fluorinated hydrocarbons) are divided to (a) chlorofluorocarbons (CFC) containing ***Cl*** and ***F*** and (b) hydrochlorofluorocarbons (HCFC) containing ***H***, ***Cl*** and ***F***. Fluorocarbons have a joint formula index $C_n(H,Cl,F)_{2n+2}$ and are used usually as cooling agent, solvent, aerosol propellant or blowing agent. The use of fluorocarbons as a densifier of drilling fluid is kept by Patent of USSR No 992562 (*Bull. Of Inventions*, 1983, Vol. 4).

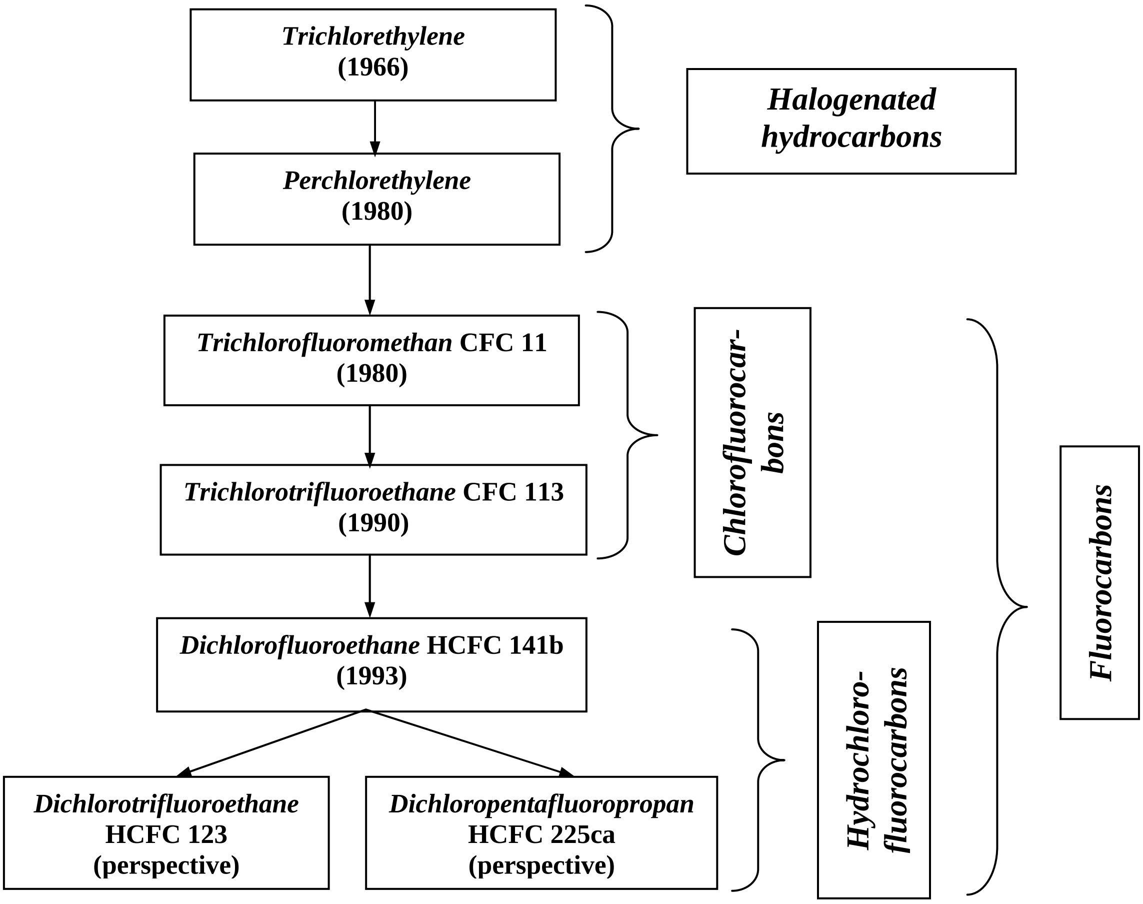
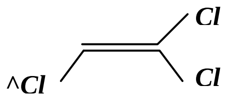
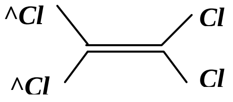
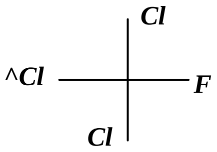
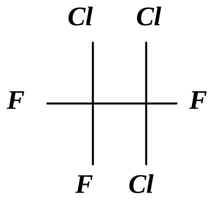
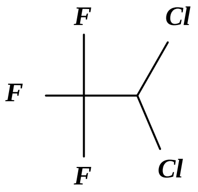
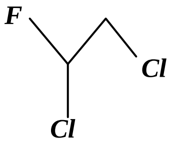


Fig.1. Densifiers for ice deep drilling (in brackets: the year of first use)

Table 2. Organic compounds – densifiers
(*Handbook of Chemistry and Physics*, 1976; *Industrial Solvents Handbook*, 1991; *Names, Synonyms, and Structures of Organic Compounds*, 1995; *Producer's data*)

Name	CAS RN*	Synonyms	Formula index	Structure	General description
Halogenated hydrocarbons					
Trichlorethylene	79-01-6	Trichlorethene; Chlorylen; Narcogen; Trieline	C_2HCl_3		Colorless, clear liquid with characteristic sweet odor of chloroform
Perchlorethylene	127-18-4	Tetrachloroethene; Didiakene; Perclene; Tetropil	C_2Cl_4		Clear, water-white liquid, ether chloroform odor
Fluorocarbons*					
Trichloro-fluoromethane	75-69-4	**CFC 11**; FC11; FREON 11; F 11; FRIGEN 11; REFRIGERANT R11; GENESOLV A	$CCl_3 F$		Clear, colorless liquid, faint ethereal odor
Trichloro-trifluoroethane	76-13-1	**CFC 113**; FC 113; FREON 113; F 113; FREON TF; FORANE 113; FLUGENE 113; ALKONE P; REFRIGERANT R113; GENENESOLV D	$C_2Cl_3F_3$		Colorless liquid, ether odor
Dichloro-trifluoroethane	354-25-6	**HCFC 123**; FC 123; FREON 123; F123; SOLKANE 123; REFRIGERANT R123	$C_2HCl_2F_3$		Colorless liquid
Dichloro-fluoroethane	430-57-9	**HCFC 141b**, FC 141b; FREON F141b; SOLKANE 141b; FORANE 141b	$C_2H_3Cl_2F$		Colorless liquid, faintly ethereal odor
Dichloro-pentafluoro-propan	306-83-2	**HCFC 225ca**; R225	$C_3HCl_2F_5$	-	Clear liquid with a slight ethereal and alcoholic odor

*__CAS RN__ is the Register Number assigned by Chemical Abstracts Service (CAS) as a unique identifier for the compound

__FREON__® is Du Pont's registered mark, **FORANE® is Elf Atochem's registered mark, **SOLKANE**® is SBU Fluorochemicals registered mark for its fluorocarbon products.

There were another candidate-densifiers, for example, polybrominated biphenyl ether and tetrabromoethane, which are not suitable with respect to their high toxicity.

Polybrominated biphenyl ether (PBBE) is a viscous semi-solid material, and it is rather hazardous to health and the environment (*Gosink et al*., 1989). The exposure levels of PBBE are very low and Environmental Protection Agency of USA lists it as extremely hazardous substance. Moreover, the brominated components of PBBE are resistant to biodegradation.

Tetrobromoethane ($C_2H_4Br_2$) belongs to the class of bromides and has extraordinary high density (2964 kg/m^3 at 20 °C). It is miscible with petroleum products (*Kudryashov et al*., 1991), but it isn't suitable for the preparation of ice core drilling fluid with respect to frost-resistance properties (freezing point of tetrabromoethane is –1 °C only) and human toxicity (threshold limit in air is 1 ppm).

Alcohols, esters and other organic liquids

The most of alcohols are hydrophilic liquids and, therefore, the technology of drilling with this kind of drilling fluid is connected mainly with dissolving of ice-cuttings or melting water. The main advantage of the alcohol's use is the decreasing of the total volume of required liquid up to 5-75 % of bore-hole volume (it depends on temperature profile).

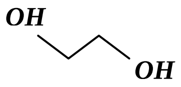
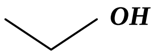
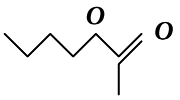
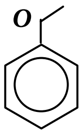
It is known the use of two types of aqueous alcohol solutions in deep ice drilling (*Table 3*): ethylene glycol solution (*Ueda and Garfield*, 1969) and ethanol solution (*Zagorodnov et al*., 1994). Aqueous solutions of ethylene glycol and ethanol have very high viscosity at negative temperatures that kept back alcohol's use in drilling at cold glaciers.

There was a proposal to use *octanol* (octyl alcohol) as a drilling fluid (*Gosink et al*., 1989; *EPICA Drilling Group*, 1994), but it is too viscous liquid (10,6 cP at 15 °C).

Ethylene glycol is a polyhydric alcohol that used usually as anti-freeze agent and solvent. Ethylene glycol is blending with water at any concentration. The freezing point of aqueous ethylene glycol solution at first reduces with concentration growth but then it increases significantly.

Ethanol is a monohydric alcohol and it is used as solvent, anti-freeze agent, jet fuel, anti-bacterial liquid and, as well as, in food industry.

Table 3. Alcohols and esters used or suitable for ice core drilling
(*Industrial Solvents Handbook*, 1991; *Names, Synonyms, and Structures of Organic Compounds*, 1995)

Name	CAS RN	Synonyms	Formula index	Structure	General description
Ethylene glycol	107-21-1	Glycol, Glycol alcohol, Ethanediol	$C_2H_4(OH)_2$		Colorless liquid with mild odor
Ethanol	64-17-5	Alcohol, Ethyl alcohol, Spirit, Tescol	C_2H_5OH		Colorless liquid with strong fragrant odor
n-Butyl acetate	123-86-4	Butyl acetate, 1-Butyl acetate, Butyl ethanoate, Acetic acid, Butyl ester	$C_6H_{12}O_2$		Water-white liquid with a characteristic fruity odor
Anisole	100-66-3	Anisol, Methoxybenzene, Phenyl methyl ether	C_7H_8O		Yellow liquid with a sweet anise-like odor

Specialists of Polar Ice Coring Office, University of Alaska, conducted a chemical literature survey in an effort to identify a ice drilling fluid with necessary viscosity and density characteristics that would minimize health and safety risks for drillers, cause minimal environmental impact, and compromise the scientific integrity of ice core. Of nearly 250 thousands compounds were electronically surveyed, and 11 potential drilling fluids were identified: *anisole*, *hexanol*, *heptanol*, *octanol*, *p-cymene*, *s-butyl benzene*, *pseudocumene*, *propyl*, *n-butyl acetate*, *amyl acetate* and *propyl proprionate.* Authors consider that of these eleven, only n-butyl acetate and anisole fully meet the requirements.

n-Butyl acetate is an ester used mainly as a solvent for nitrocellulose and cellulose industry. There are two main disadvantages of n-butyl acetate use: it is rather hazardous to human health and it is the very aggressive solvent (it dissolves oils, fates, waxes, metallic resinates, camphor, rubber, synthetic resins, and many other substances).

Density of n-butyl acetate is near 930 kg/m^3 at –30 °C, and for drilling in cold glaciers an adding of densifier will not be required. For more temperate glacier drilling operations *Gosink et al*. (1989) suggested to use mixture of n-butyl acetate with 10 % of anisole as densifier.

Anisole is used in perfumery and as solvent in a variety of other uses. It isn’t miscible with water but blends in alcohol, ether and benzol in any concentration. Probably anisole is much more desirable than other densifiers with respect to human toxicity and environmental pollution but it had never been used in practice of ice drilling.

Silicon oils

Silicon oils are used in industry as a hydraulic liquids and lubricants, as well as, on movie films, gramophones, records, plastics, etc. Silicon oils are hydrophobic and inert substances that are stable to water, air, oxygen, metals, wood, paper, plastics. Silicone oils have good toxicological and environmental properties, they are absolutely safety for human health.

The most suitable kind of silicon oils for deep ice drilling are ***dimethyl siloxane oils*** (*Table 4*) that differ from other silicon, mineral and synthetic fluids by the most little viscosity changes with temperature variation. Dimethyl siloxane oils can work for a long period at temperatures from –60 to –100 °C.

Table 4. Silicon oils (dimethyl siloxane oils) as ice drilling fluids

Name	**CAS RN**	**Synonyms***	**Formula index**	**General description**
Decamethyl tetrasiloxane	141-62-8	KF96-1,5cs; PMS-1,5p	$(CH_3)_{10}Si_4O_3$	Clear water-white, tasteless, odorless and neutral liquid
Dodecamethyl pentasiloxane	141-63-9	KF96-2,0cs; PMS-2,0p	$(CH_3)_{12}Si_5O_4$	The same
Tetradecamethyl hexasiloxane	107-52-8	KF96-2,5cs; PMS-2,5p	$(CH_3)_{14}Si_6O_5$	The same

*KF96 is a trade mark of Shin-Etsu Chemical Co.;
PMS is an abbreviation of polymethyl siloxane oils used in Russia

At first, the suggestion to use silicon oil as drilling fluid was made by *Fujita et al*., 1994, but authors noticed that “it has a higher viscosity than the other candidates and it is expensive”.

2. DENSITY AND FLUID TOP

General considerations

In references we can find the following recommendations for the choice of the fluid density:

- 920-950 kg/m^3 at temperatures between –10 and –32 °C (*Gundestrup et al*., 1994a);
- 920 kg/m^3 (*Gosink et al*., 1994);
- 940-960 kg/m^3 (*Fujita et al*., 1994);
- 935-940 kg/m^3 at the fluid top 100 m (*Litvinenko et al*., 1996).

The choice of the fluid density should be done from the view of pressure difference between fluid and ice. According to Pascal's principle the pressure applied at any point of a fluid at rest is transmitted without loss to all other parts of the fluid.

The pressure P [Pa] in a bore-hole fluid at the rest condition follows from the main hydrostatic equation:

$$\frac{dP}{dz} = -g\rho, \qquad (1)$$

where z is the height, m; g is the acceleration of gravity, m/s^2; ρ is the density, kg/m^3.

The variables in formula (1) are the density and the height. These parameters determine the pressure of fluid on the bottom and the walls of the bore-hole.

The fluid density $\rho_{fl}(z)$ and ice density $\rho_{ice}(z)$ depends both on the temperature and the pressure in the bore-hole. With increasing temperature the density decreases and with increasing pressure the density increases too.

In practice the density varies with depth, and the hydrostatic pressure $P_{fl}(z)$ and overburden pressure of ice $P_{ice}(z)$ at the depth H [m] can be found by integration of equation (1):

$$P_{fl}(z) = \begin{cases} 0, & 0 < z < H_0 \\ g\int_{Ho}^{H} \rho_{fl}(z)dz, & H_0 < z < H \end{cases} \qquad (2)$$

$$P_{ice}(z) = g\int_{0}^{H} \rho_{ice}(z)dz\ , \qquad (3)$$

where $\rho_{fl}(z)$ and $\rho_{ice}(z)$ are the density profile in bore-hole of fluid and ice respectively, kg/m^3; H_0 is the fluid top, m (*Fig. 1*).

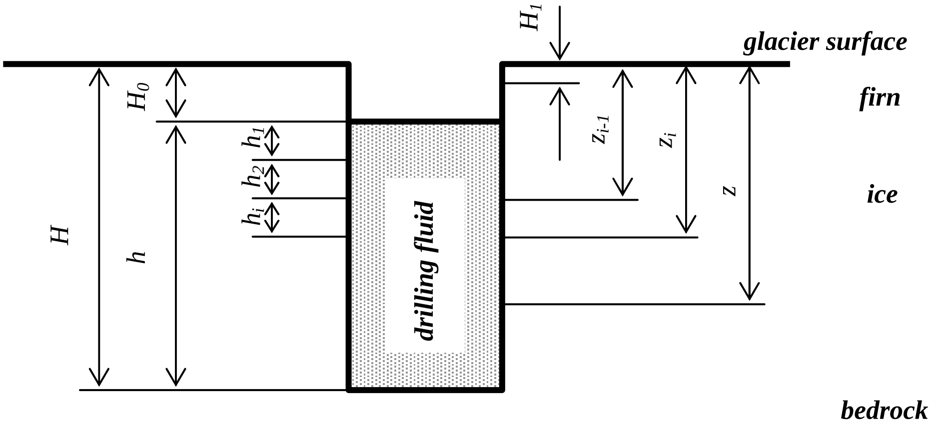


Fig.1 Scheme of the bore-hole

Then the pressure difference between the hydrostatic pressure of fluid and the ice-overburden pressure $\Delta P(z)$ can be found:

$$\Delta P(z) = P_{fl}(z) - P_{ice}(z), \tag{4a}$$

or

$$\Delta P(z) = g\int_0^H \left[\rho_{fl}(z) - \rho_{ice}(z)\right] dz\,. \tag{4b}$$

Thus, the pressure difference in the bore-hole is a function from depth, and its value depends from the densities profile $\rho_{fl}(z)$ and $\rho_{ice}(z)$. Theoretically we can observe three kinds of the pressure difference:

1) negative pressure difference $\Delta P(z) < 0$;
2) pressure equilibrium $\Delta P(z) = 0$;
3) positive pressure difference $\Delta P(z) > 0$.

One of the most important functions of the fluid using for ice deep drilling is the prevention of the bore-hole closure. The prevention of the bore-hole closure is achieved in the second and the third cases:

$$\int_0^H \left[\rho_{fl}(z) - \rho_{ice}(z)\right] dz \geq 0\,. \tag{5}$$

The best way is to ensure $\rho_{fl}(z) = \rho_{ice}(z)$, but in practice it is rather difficult because the expansion coefficient and the compressibility of fluids and ice are rather different.

Fluid top

The fluid top can't be at the surface of the glacier. First of all the upper interval of the most glaciers and ice caps is permeable, and the other reason is the rising of fluid level during lowering down of the drill and cable.

The rising of the fluid top ΔH_0 during drill lowering down depends on the diameter of the cable d_c, volume of the drill V_d and the diameter of the upper part of the bore-hole D_h:

$$\Delta H_0 = \left(\frac{d_c}{D_h} \right)^2 (z - H_0) + \frac{4V_d}{\pi D_h^2} \,. \tag{6}$$

In most cases the rising of the fluid top doesn't exceed of 15 – 25 m.

The depth of the permeable zone depends on the accumulation rate and temperature conditions of the glacier. It is considered, that firn becomes ice, when its density reached at a value of 830 kg/m^3. *Table 2* lists the depth of the firn-ice transition at different polar regions.

Table 2. Depth of firn-ice transition (Paterson, 1994; *Gow et al.,* 1997 *)*

Polar site	**Depth, m**
Antarctica	
South Pole	115
Vostok Station	95
Dome C	100
Byrd Station	64
Greenland	
Camp Century	68
Dye 3	65-70
Summit	75-77

Due to the environmental requirements the permeable firn zone is isolated with casing. For the prevention of the leaks at the bottom of the casing a special thermal or mechanical devices are used. If the fluid top is rather higher than the bottom of the casing, there is the high risk of leaks. Therefore the top of the drilling fluid is at 40 – 100 m usually.

Density profile of ice

The upper part of glaciers contains a lot of air inclusions and the ice density smoothly increases with depth. An empirical density-depth relation can be found according to (*Schytt*, 1958):

$$\rho_{ice}(z) = \rho_{ice} - (\rho_{ice} - \rho_{sn})\exp(-Cz) \ , \tag{7}$$

where ρ_{sn} is the density of surface snow (300 – 400 kg/m^3); C is the empirical coefficient (C = 0,016-0,031 m^{-1}; *Paterson*, 1994).

The ice density ρ_{ice} can be estimated according to (summaries from *Hobbs*, 1974):

$$\rho_{ice} = 916{,}8\frac{(1 - 1{,}53\times10^{-4}t)}{1 - 11{,}94\times10^{-11}(1 + 1{,}653\times10^{-3}t + 3{,}12\times10^{-6}t^2)(P - P_0)} . \tag{8}$$

where t is the temperature, °C; P is the pressure, Pa; P_0 is the standard atmospheric pressure ($P_0 = 1{,}013\cdot10^5$ Pa).

As a result of pressure growth and compression of air bubbles the ice density increases with depth. The temperature usually increases with depth also and the thermal expansion may more offset the effect of pressure on density.

For example, at Byrd Station (Antarctica) the density reaches a maximum of 920,6 kg/m^3 at a depth of 1000 m and then decreases to 917 kg/m^3 at 2164 m (*Gow*, 1971). At Summit (Greenland) the density reaches the maximal value of 920,8 kg/m^3 in completely bubble-free ice at around of 1600 m and decreases progressively to the 917,2 kg/m^3 at 3040 m (*Gow et al.*, 1997).

The experimental density profiles at Vostok station were obtained independently with two different techniques by hydrostatic weighing and volumetric method (*Lipenkov et al.*, 1997). The density smoothly increases from 918 kg/m^3 at the depth 200 m to 924 kg/m^3 at 1000 m, and then the density decreases to 921 kg/m^3 at 2600 m.

Generally the influence of the pressure and of the temperature is compensated mutually, and the density of ice may be taken constant at an average value. At Vostok Station the average density of ice is 923 kg/m^3 up to the depth of 3000 m (*V.Lipenkov*, personal communication); in Central Greenland the average density of ice can be taken as 920 kg/m^3 (*Gundestrup et al.*, 1994b).

Using the average value of ice density $\bar{\rho}_{ice}$ and accounting the difference between the average density of ice and the density of upper snow-firn zone with density less than average, equation (3) gives:

$$P_{ice}(z) = \bar{\rho}_{ice} g(z - H_1) . \tag{9}$$

The height H_1 often is named as firn correction and its value depends on the ice accumulation conditions. For example, at Vostok Station firn correction is 34 m (*Tchistyakov et al.*, 1994); at Central Greenland firn correction is 24 m (*Gundestrup et al.*, 1994b).

Approximate density profile of fluid

Frequently the fluid compressibility is neglected, possibly because it is difficult to measure. Neglecting compressibility the fluid density $\rho_{fl}^{t}(z)$ at the temperature t [°C] is determined using the thermal expansion coefficient k_t [K^{-1}]:

$$\rho_{fl}^{t}(z) = \frac{\rho_0}{1 + k_t (t - t_0)} , \tag{10}$$

where ρ_0 is the density of the fluid at temperature t_0.

Equation (10) is inconvenient because the thermal expansion coefficient k_t isn't constant and changes with temperature too. For limited range of temperatures the density can be approximated with linear equation and may defined by Mendeleeff's formula:

$$\rho_{fl}^{t}(z) = a_t (t - t_0) + \rho_0 , \tag{11}$$

or

$$\rho_{fl}^{t}(z) = a_t t + b , \tag{12}$$

where a_t is the thermal coefficient, kg/(m^3·°C); b is the density of fluid at 0 °C.

Density-temperature relation of some fluids (for example, aqueous solutions of alcohols) isn't linear. In this case the quadratic equation can be used:

$$\rho_{fl}^{t}(z) = a_t t^2 + b_t t + c , \tag{13}$$

where a_t and b_t are the empirical coefficients; c is the density of fluid at 0 °C, kg/m^3.

The equations for the density of drilling fluids for deep ice core drilling *versus* temperature are represented in *Table 3*.

Table 3. Density [kg/m^3] of the drilling fluids under atmospheric pressure

Name	**Density (specification) / at temperature [°C]**	**Density *versus* temperature [°C]**	**Temperature interval, °C**	**Expansion coefficient*, 10^{-3} K^{-1}**	**References**
Petroleum products					
Fuel DF-A	770-840/ at 15	$\rho_{fl}^t = -0,673t + 816,5$	-41/19	0,80	*N.Gundestrup*, unpublished
Fuel TS-1	776-786/ at 20	$\rho_{fl}^t = -0,765t + 796$	-55/0	0,93	*V.Lipenkov*, unpublished
		$\rho_{fl}^t = -0,749t + 810,2$	-52/-6	0,90	*Litvinenko et al.*, 1996
Fuel Jet A-1	775-840/ at 15	$\rho_{fl}^t = -0,668t + 826,0$	-30/20	0,79	*Gundestrup et al.*, 1984
Fuel JP-8	775-830/ at 15	$\rho_{fl}^t = -0,753t + 818,4$	-50/0	0,89	*Litvinenko et al.*, 1996
Solvent IP-1200	-	$\rho_{fl}^t = -0,92t + 770$	-60/0	1,15	*Fujita et al.*, 1994
Exxol D60	788/ at 15	$\rho_{fl}^t = -0,737t + 804,1$	-35/0	0,91	*Producer's data*, 1998
		$\rho_{fl}^t = -0,712t + 800,1$	-56/22	0,92	*P.Talalay*, unpublished
Exxol D40	771/ at 15	$\rho_{fl}^t = -0,693t + 778,2$	-57/22	0,87	*P.Talalay*, unpublished
Exxol D30	758/ at 15	$\rho_{fl}^t = -0,726t + 767$	-57/22	0,92	*P.Talalay*, unpublished
Densifiers – ethylene hydrocarbons					
Trichlorethylene	1464/ at 20	$\rho_{fl}^t = -1,62t + 1495$	-50/20	1,04	*Promyshlennye hlororganicheskiye soedineniya*, 1978
Perchlorethylene	1625/ at 20	$\rho_{fl}^t = -1,575t + 1656,5$	-20/20	0,93	*Promyshlennye hlororganicheskiye soedineniya*, 1978
Densifiers - chlorofluorocarbons					
CFC 11	1487/ at 20	$\rho_{fl}^t = -2,202t + 1534,4$	-47/-10	1,37	*Litvinenko et al.*, 1996
CFC 113	1570/ at 25	-	-	-	*EPICA Drilling Group*, 1994
HCFC 123	1480/ at 20	$\rho_{fl}^t = -2,379t + 1526,2$	-30/0	1,49	*Producer's data*, 1998
		$\rho_{fl}^t = -2,21t + 1527,8$	-58/22	1,39	*P.Talalay*, unpublished
HCFC 141b	1240/ at 20	$\rho_{fl}^t = -0,0033t^2 - 1,631t + 1279,1$	-60/0	1,04	*Producer's data*
		$\rho_{fl}^t = -1,76t + 1282,7$	-50/-10	1,32	*V.Lipenkov*, unpublished
		$\rho_{fl}^t = -1,733t + 1280,5$	-57/23	1,30	*P.Talalay*, unpublished
HCFC 225ca	1543/ at 25	-	-	-	*EPICA Drilling Group*, 1994
Alcohols, ethers and other organic liquids					
Ethylene glycol	1115,5/ at 20	$\rho_{fl}^t = -0,694t + 1127,3$	-12/40	0,61	*Industrial Solvents Handbook*, 1991

Ethanol	789,3/ at 20	$\rho_{fl}^t = -0,844t + 806,3$	0/39	1,01	*Handbook of Chemistry and Physics*, 1976
n-Butyl acetate	882/ at 20	$\rho_{fl}^t = 0,0116t^2 - 0,982t + 895$	-50/20	1,4	*Gosink et al.*, 1994
		$\rho_{fl}^t = -0,97t + 901,3$	-57/23	1,04	*P.Talalay*, unpublished
Anisole	995,4/ at 20	$\rho_{fl}^t = 0,0174t^2 - 0,697t + 1003,2$	-35/20	1,2	*Gosink et al.*, 1994
Aqueous solutions of alcohols					
Aqueous ethylene glycol solution (C_M = 0,4)	1056/ at 10	$\rho_{fl}^t = -0,0023t^2 - 0,372t + 1060,3$	-23/40	-	*Industrial Solvents Handbook*,1991
Aqueous ethylene glycol solution (C_M = 0,6)	1083/ at 10	$\rho_{fl}^t = -0,0015t^2 - 0,541t + 1088,4$	-45/40	-	*Industrial Solvents Handbook*,1991
Aqueous ethylene glycol solution (C_M = 0,8)	1105/ at 10	$\rho_{fl}^t = -0,0015t^2 - 0,636t + 1110,9$	-45/40	-	*Industrial Solvents Handbook*,1991
Aqueous ethanol solution (C_M = 0,4)	935,2/ at 20	-	-	-	*Handbook of Chemistry and Physics*, 1976
Aqueous ethanol solution (C_M = 0,6)	891,1/ at 20	-	-	-	*Handbook of Chemistry and Physics*, 1976
Aqueous ethanol solution (C_M = 0,8)	843,6/ at 20	-	-	-	*Handbook of Chemistry and Physics*, 1976
Aqueous ethanol solution at freezing point	-	$\rho_{fl}^t = -0,026t^2 - 0,414t + 974,3$	-53/-13	-	*Gosink et al.*, 1994
Silicon oils					
KF96-1,5cs	850-855/ at 25	$\rho_{fl}^t = -t + 874,2$	-30/20	1,1	*Fujita et al.*, 1994
KF96-2,0cs	870-875/ at 25	$\rho_{fl}^t = -0,968t + 894,2$	-58/23	1,05	*P.Talalay*, unpublished

*Calculated average value at temperatures from –30 to 0 °C

Experiments carried out in Copenhagen University showed that density of n-butyl acetate is equal to the ice density at –19 °C and the density of silicon oil KF96-2,0cs is equal to the ice density at –27 °C (*Fig. 2*). In a result of these measurements linear density-temperature relation of n-butyl acetate was obtained in defiance of parabolic relation used by PICO, University of Alaska (*Gosink et al.*, 1991).

The temperature profile in glacier depends on average surface temperature, present variation of temperature, geothermal heat, friction and other factors. Due to the internal temperature glaciers are deviated to *cold glaciers*, in which all ice is below melting point and melting point is reached only at the bed, and *temperate glaciers*, in which all ice, except the surface layer, is at melting point. The temperature profiles at some polar sites are represented in *Table 4*.

Fig. 2. Density of n-butyl acetate and silicon oil KF96-2,0cs versus temperature

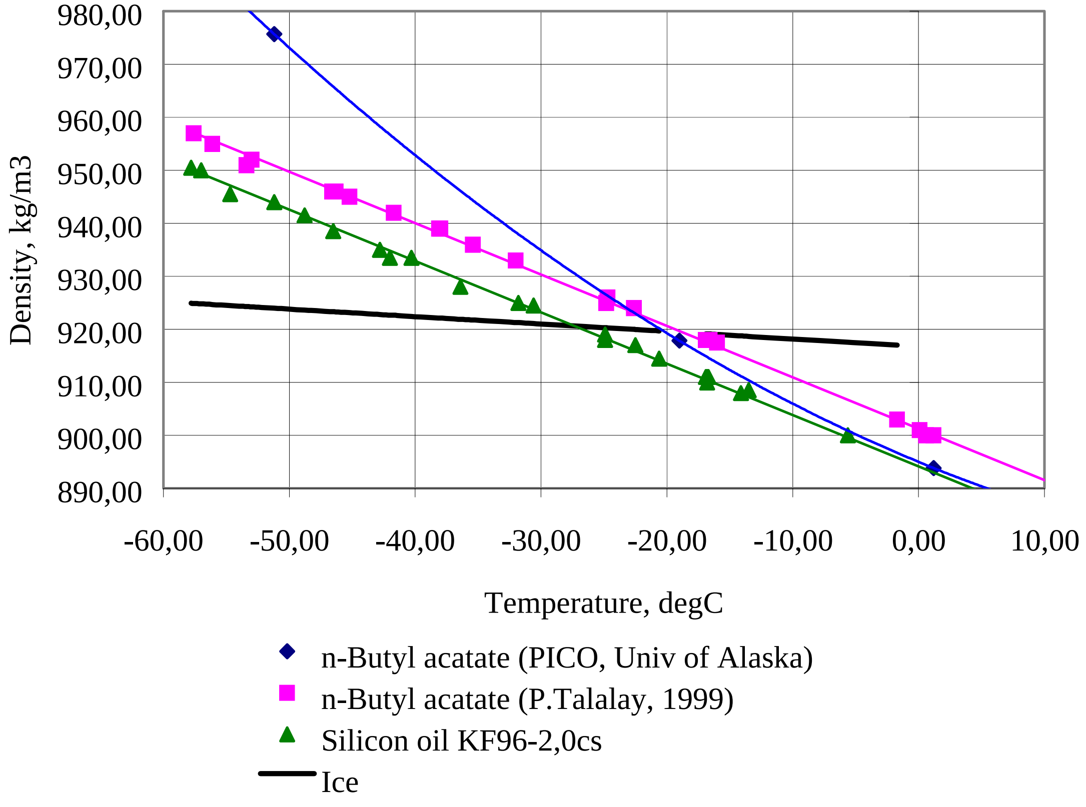


Table 4. Temperature profiles at four drilling sites of Antarctica and Greenland

Polar site	**Temperature [°C] *versus* depth [m]**	**Interval, m**	**References**
Antarctica			
Vostok Station	$t = -56,15 + 6,5493 \cdot 10^{-3} z + 1,1829 \cdot 10^{-6} z^2 + 3,7477 \cdot 10^{-10} z^3$	100 - 3300	*Tchistyakov et al.*, 1994
Dome C	$t = -54,46 + 4,9664 \cdot 10^{-3} z + 3,7539 \cdot 10^{-6} z^2 - 3,81 \cdot 10^{-11} z^3$	100 - 3000	*S.J.Johnsen*, personal communication
Central Greenland			
Summit Camp GRIP	$t = -31,84 + 3,236 \cdot 10^{-3} z - 6,0511 \cdot 10^{-6} z^2 + 2,5242 \cdot 10^{-9} z^3$	45 - 3026	*Gundestrup et al.*, 1994b
Summit Camp GISP2	$t = -31,46 + 2,9257 \cdot 10^{-3} z - 5,6474 \cdot 10^{-6} z^2 + 2,3451 \cdot 10^{-9} z^3$	102 - 3046	*N.S. Gundestrup* , unpublished

In order to calculate the hydrostatic pressure, we first need to estimate the temperature profile at the drilling site. Then using the temperature profile the density *versus* depth is calculated, and the hydrostatic pressure can be found using the approximately integration method of trapezium:

$$P_{fl}^{t}(z) = g\sum \frac{\rho_{fl}^{t}(z_{i-1}) + \rho_{fl}^{t}(z_i)}{2} h_i \,. \tag{14}$$

where h_i is the depth interval.

For shallow and intermediate drillings, equation (14) gives satisfactory results. For deep drillings however the neglecting of the fluid compressibility leads to significant errors. *Kuksov et al.* (1992), for example, found the pressure error of about 6 % in an oil well when the compressibility is ignored. For the GISP bore-hole using the n-butyl acetate *Gosink et al.* (1991) found the density to increase 3 % at the bottom of the 3-km bore-hole due to the pressure.

Real density profile of fluid

There are several methods to estimate the hydrostatic pressure in a compressible fluid. The most widespread equation is (*Kuksov et al.*, 1992)

$$P_{fl}^{P,t}(z) = kP_{fl}^{t}(z) \,, \tag{15}$$

where $P_{fl}^{P,t}(z)$ is the hydrostatic pressure corrected for both thermal expansion and compressibility of the fluid; k is the coefficient accounting compressibility of the fluid.

According to equation (15) we can’t calculate the hydrostatic pressure exactly because the value of the coefficient k isn’t constant, it depends on type of the bore-hole fluid, pressure and temperature.

At constant temperature and changing pressure P the density is

$$\rho_{fl}^{P} = \frac{\rho_0}{1 - k_P(P - P_0)} \,, \tag{16}$$

where k_P is the compressibility of the fluid, Pa^{-1}; ρ_0 is the density of the fluid under the pressure P_0.

The calculation of the real fluid density profile may be done in two stages (*Menshikov and Talalay*, 1993). The first stage includes the calculation of the density $\rho_{fl}^{t}(z)$ at real temperatures in bore-hole and standard atmospheric pressure using equations (10), (11), or (12). Next the density is corrected for the real pressures in bore-hole:

$$\rho_{fl}^{P,t}(z) = \frac{\rho_{fl}^{t}(z)}{1 - k_P P_{fl}(z)} \,. \tag{17}$$

In this case the hydrostatic pressure of fluid $P_{fl}^{P,t}(z)$ at the depth z is calculated step by step using the approximately integration method of rectangle:

$$P_{fl}^{P,t}(z) = g \sum \rho_{fl}^{P,t}(z_{i-1}) h_i \ , \tag{18}$$

Here we can't use the more correct method of trapezium because the density at the depth z_i depends on the pressure itself and is unknown.

The simultaneous accounting of the temperature and the pressure on the hydrostatic pressure may be done according to following equation (*Blinov and Talalay,* 1998):

$$P_{fl}^{P,t}(z) = \frac{1}{2k_P}\left\{1 + k_P P_0 - \sqrt{(1-k_P P_0)^2 - 4k_P \rho_0 g \int_{H_0}^{H} \frac{1}{1+k_t(t-t_0)}\left[1 - \frac{k_t z}{1+k_t(t-t_0)}\frac{dt}{dz}\right]dz}\right\}, \tag{19}$$

where ρ_0 is the density of fluid at the temperature t_0 [°C] and the pressure P_0 [Pa], kg/m^3; dt/dz is the temperature gradient in bore-hole, °C/m.

For the correct calculation according to equations (17) or (19) it is necessary to know the exact value of the fluid compressibility k_P, which significantly depends on the temperature and pressure. For solids values of compressibility are typically of the order 10^{-11} Pa^{-1}, and for liquids 10^{-9} Pa^{-1} (*Table 5*). With increasing pressure and lowing temperature liquid compressibility approaches the values for solids.

Table 5. Fluids compressibility versus temperature [°C]

Name	Compressibility, Pa^{-1}	Interval of absolute pressure, MPa	References
Fuel TS-1	$k_P = (0,0106\ t + 0,7093) \cdot 10^{-9}$	0,1 - 10	*Dubovkin et al.*, 1985
CHC 11	$k_P = (0,0082\ t + 1,331) \cdot 10^{-9}$	0,1 - 20	*Bogdanov et al.*, 1976
n-Butyl acetate	$k_P = (-4,72t + 1091,7)^{-1} \cdot 10^{-6}$	0,1 - 30	*Eastman Chemical Co.* (USA), 1990

The value of compressibility can be calculated due to the value of bulk modulus. Fluids, as well as solids, have bulk modulus, and compressibility is reciprocal to the bulk modulus. Bulk modulus depends on temperature and pressure also. According to Eastman Chemical Co. (USA) the bulk modulus of n-butyl acetate is equal to 1238,15 MPa at temperature –31 °C and 1068,13 MPa at 5 °C. The compressibility of n-butyl acetate *versus* temperature was approximated according to the linear relationship (*Table 5*).

Sometimes, the real fluid density profile can be calculated using empirical density-temperature-pressure equations, for example, such as in *Table 6*.

Table 6. Fluids density versus temperature t [°C] *and absolute pressure P* [MPa]

Name	**Density, kg/m^3**	**Temperature and pressure intervals**	**Refer-ences**
Solvent Exxol D60	$\rho_{fl}^{P,t} = 804{,}1 - 0{,}739t + (0{,}7113 + 1{,}665 \times 10^{-3} t)P$	-35 ≤ t ≤ 0 °C 0,1 ≤ P ≤ 30 MPa	*Producer's data*, 1998
HCFC 123	$\rho_{fl}^{P,t} = 1527{,}8 - 2{,}35t + (1{,}89 + 0{,}013t)P$	-30 ≤ t ≤ 0 °C 0,1 ≤ P ≤ 30 MPa	*Producer's data*, 1998
Silicon oil KF96-2,0	$\rho_{fl}^{P,t} = \frac{891{,}6 - 1{,}08t}{1 - 10^{-5} t\left[0{,}52(P - P_0) + 6{,}1\right] - 10^{-3}(P - P_0) - 2{,}05 \times 10^{-3}}$	-50 ≤ t ≤ 25 °C 0,1 ≤ P ≤ 35 MPa	*Producer's data*, 1998

Density profile of two-compound fluid

In the following it is assumed that the two components in the fluid don't react neither chemically nor physically.

For the preparation of two-compound fluid with the density ρ_{fl} the volume of densifier V_2 at given temperature is estimated according to:

$$V_2 = V \frac{\rho_{fl} - \rho_1}{\rho_2 - \rho_1}, \tag{20}$$

where V is the volume of mixture, m^3; ρ_1 and ρ_2 are the density of the base fluid and the densifier respectively, kg/m^3.

The density of mixture at atmospheric pressure is

$$\rho_{fl} = (1 - C_V)\rho_1 + C_V \rho_2, \tag{21}$$

or

$$\rho_{fl} = \frac{\rho_1}{1 - C_M \frac{\rho_2 - \rho_1}{\rho_2}}, \tag{22}$$

where C_V and C_M are the volume and mass concentration of densifier respectively, parts of unity.

The volume and mass concentrations can be calculated due to the following equations:

$$C_V = \frac{\rho_{fl} - \rho_1}{\rho_2 - \rho_1}; \tag{23}$$

$$C_M = \frac{\rho_2(\rho_{fl} - \rho_1)}{\rho_{fl}(\rho_2 - \rho_1)}. \tag{24}$$

The volume concentration slightly depends from the temperature, therefore, it's opportune to use the mass concentration. The relation between volume and mass concentrations is following:

$$C_V = C_M \frac{\rho_{fl}}{\rho_2}; \tag{25}$$

or

$$C_V = \left[\frac{\rho_2}{\rho_1}\left(\frac{1}{C_M} + 1\right)\right]^{-1}. \tag{26}$$

Based on equations (21) or (22) the change of mixture's density with temperature and pressure can be calculated knowing how the density of the two components changes. Equation (22) leads to the following density profile of two-compound fluid:

$$\rho_{fl}^{P,t}(z) = \frac{\rho_1^{P,t}(z)}{1 - C_M \dfrac{\rho_2^{P,t}(z) - \rho_1^{P,t}(z)}{\rho_2^{P,t}(z)}}. \tag{27}$$

Then the hydrostatic pressure of the fluid $P_{fl}^{P,t}(z)$ can be calculated using equation (18).

The condition for no-reaction between the two components is verified for mixture of fuel TS-1 (base fluid) with trichlorofluoromethane (CHC 11) as densifier. The density of the fuel TS-1 $\rho_1^t(z)$ and the density of the densifier CHC 11 $\rho_2^t(z)$ *versus* temperature are (*Litvinenko et al*., 1996):

$$\rho_1^t(z) = -0{,}749t + 810{,}2; \tag{28}$$

$$\rho_2^t(z) = -2{,}202t + 1534{,}4; \tag{29}$$

Equations (28) and (29) are substituted in (27), and the density of the mixture is obtained:

$$\rho_{fl} = \frac{810{,}2 - 0{,}749t}{1 - \dfrac{C_M(724{,}2 - 1{,}453t)}{1534{,}4 - 2{,}202t}}. \tag{30}$$

The results are compared with experimental data (*Table 7*). The difference between measured and calculated densities of isn't more than 0,5 %. Thus, we can conclude that for this mixture the two components don’t react and the density can be calculated using the densities of the compounds.

Table 7. Density [kg/m^3] versus temperature [°C] of fuel TS-1 with densifier CHC 11

Mass concentration C_M	**Experimental equations** (*V.Lipenkov,* unpublished*)*	**Theoretical equations due to (31)**	**Maximal difference in the range from –50 to 0 °C, %**
0,02	$\rho_{fl} = -0{,}768t + 818{,}3$	$\rho_{fl} = -0{,}761t + 817{,}9$	0,09
0,04	$\rho_{fl} = -0{,}824t + 824{,}2$	$\rho_{fl} = -0{,}772t + 825{,}8$	0,19
0,06	$\rho_{fl} = -0{,}831t + 832{,}4$	$\rho_{fl} = -0{,}784t + 833{,}8$	0,17
0,10	$\rho_{fl} = -0{,}835t + 847{,}1$	$\rho_{fl} = -0{,}810t + 850{,}3$	0,38
0,14	$\rho_{fl} = -0{,}901t + 865{,}1$	$\rho_{fl} = -0{,}836t + 867{,}5$	0,28
0,18	$\rho_{fl} = -0{,}924t + 882{,}5$	$\rho_{fl} = -0{,}865t + 885{,}4$	0,33
0,22	$\rho_{fl} = -0{,}938t + 901{,}6$	$\rho_{fl} = -0{,}894t + 904{,}1$	0,27
0,26	$\rho_{fl} = -0{,}999t + 919{,}5$	$\rho_{fl} = -0{,}926t + 923{,}5$	0,43
0,30	$\rho_{fl} = -1{,}060t + 939{,}3$	$\rho_{fl} = -0{,}960t + 943{,}8$	0,48

The analogous comparisons of tests and theoretical estimations were done for the mixtures of solvents Exxol D60 and D30 with densifiers HCFC 141b and HCFC 123 (*Table 8*). Experimental and theoretical equations are in good agreement confirming that these compounds are in the condition of no-reaction too. The summarizing of this method for different kind of mixtures is given in *Table 9*.

Table 8. Experimental and theoretical density-temperature equations for mixtures of solvents Exxol D60 and D30 with densifiers HCFC 141b and HCFC 123

Compounds		**Tests**		**Theoretical method**		**Maximal difference in the range from –30 to 0 °C^1 from –50 to 0 °C^2, %**
Base fluid	**Densifier (concentration)**	**Experimental equations**	**Density at -30 °C^1 -50 °C^2, kg/m^3**	**Theoretical equations**	**Density at -30 °C^1 -50 °C^2, kg/m^3**	
Exxol D60	**HCFC 141b (C_M=0,317)**	$\rho_{fl}=-0{,}896t+905{,}8$	932,7^1	$\rho_{fl}=-0{,}899t+908{,}0$	935,0^1	0,24^1
Exxol D60	**HCFC 123 (C_M=0,25)**	$\rho_{fl}=-0{,}878t+906{,}1$	932,5^1	$\rho_{fl}=-0{,}881t+908{,}6$	935,0^1	0,27^1
Exxol D30	**HCFC 141b (C_M=0,342)**	$\rho_{fl}=-0{,}873t+890{,}6$	934,3^2	$\rho_{fl}=-0{,}923t+888{,}8$	935,0^2	0,20^2
Exxol D30	**HCFC 123 (C_M=0,276)**	$\rho_{fl}=-0{,}921t+888{,}3$	934,4^2	$\rho_{fl}=-0{,}911t+899{,}4$	935,0^2	0,12^2

Table 9. Theoretical equations of density [kg/m^3] of two-compound fluids versus temperature [°C] and concentration [parts of unity]

Compounds		**Equations**
Base fluid	**Densifier**	
Fuel TS-1	**CFC 11**	ρ_{fl} = 810,2 – (0,749 + 1,453 C_V) t + 724,2C_V ; $\rho_{fl} = \dfrac{810{,}2 - 0{,}749t}{1 - \dfrac{C_M(724{,}2 - 1{,}453t)}{1534{,}4 - 2{,}202t}}$
Fuel TS-1	**HCFC 141b**	ρ_{fl} = 810,2 – (0,749 + 1,011 C_V) t + 472,5C_V ; $\rho_{fl} = \dfrac{810{,}2 - 0{,}749t}{1 - \dfrac{C_M(472{,}5 - 1{,}011t)}{1282{,}7 - 1{,}76t}}$
Exxol D60	**HCFC 141b**	ρ_{fl} = 800,1 – (0,711 + 1,022 C_V) t + 480,4C_V ; $\rho_{fl} = \dfrac{800{,}1 - 0{,}711t}{1 - \dfrac{C_M(480{,}4 - 1{,}022t)}{1280{,}5 - 1{,}733t}}$
Exxol D60	**HCFC 123**	ρ_{fl} = 800,1 – (0,711 + 1,499 C_V) t + 727,7C_V ; $\rho_{fl} = \dfrac{800{,}1 - 0{,}711t}{1 - \dfrac{C_M(727{,}7 - 1{,}499t)}{1527{,}8 - 2{,}21t}}$
Exxol D30	**HCFC 141b**	ρ_{fl} = 767 – (0,726 + 1,007 C_V) t + 513,5C_V ; $\rho_{fl} = \dfrac{767 - 0{,}726t}{1 - \dfrac{C_M(513{,}5 - 1{,}007t)}{1280{,}5 - 1{,}733t}}$
Exxol D30	**HCFC 123**	ρ_{fl} = 767 – (0,726 + 1,484 C_V) t + 760,8C_V ; $\rho_{fl} = \dfrac{767 - 0{,}726t}{1 - \dfrac{C_M(760{,}8 - 1{,}484t)}{1527{,}8 - 2{,}21t}}$

The experimental density-temperature equations for some drilling mixtures from literature data are represented in *Table 10.*

The density of aqueous solutions of hydrophilic liquids doesn't submitted to equations (21) and (22) because of their molecular reconstruction in the mixture. For example, density of aqueous ethanol solutions at 20 °C can be found according to (Handbook of Chemistry and Physics, 1976):

$$\rho_{fl} = -79{,}03\ C_M^2 - 130{,}16\ C_M + 998{,}5; \qquad (31)$$

and density of aqueous ethylene glycol solutions at 21,1 °C:

$$\rho_{fl} = -34{,}15\ C_M^2 - 151{,}7\ C_M + 996{,}5. \qquad (32)$$

Table 10. Experimental density-temperature equations for different drilling mixtures

Compounds		**Equations**	**Temperature interval, °C**	**References**
Base fluid	**Densifier (concentration)**			
Fuel DF-A	**Perchlorethylene (C_V=0,103)**	ρ_{fl}=-0,719t+891,9	-41/25	*N.Gundestrup*, unpublished
Fuel Jet A1	**Perchlorethylene** (C_V=0,103)	ρ_{fl}=-0,807t+897,8	-30/20	*N.Gundestrup*, unpublished
Fuel TS-1	**Trichlorethylene** (C_M=0,214)	ρ_{fl}=-0,749t+873,4	-60/0	*Pashkevich and Chistyakov*, 1989
Solvent IP-1200	**CFC 11** (C=0,2)	ρ_{fl}=-1,05t+908,0	-55/-5	*Fijita et al.*, 1994
n-Butyl acetate	**Anisole** (C=0,1)	ρ_{fl}=0,0137t^2-0,904t+895	-50/20	*Gosink et al.*, 1994

In practice it is difficult to mix the two components with the sufficient accuracy, and *in situ* measurements are needed to verify the density profile. One possibility is to take samples from different depths of the bore-hole. At the surface the density of the sample is measured under atmospheric pressure at fixed temperature and the mass concentration of densifier in the sample from the depth z is calculated:

$$C_M = \frac{\rho_2^t(z)\left[\rho_{fl}^t(z) - \rho_1^t(z)\right]}{\rho_{fl}^t(z)\left[\rho_2^t(z) - \rho_1^t(z)\right]}. \qquad (33)$$

Then the real density according to equation (27) can be found.

Hydrostatic pressure and density profile in GISP2 bore-hole at Summit, Greenland

In 1990 – 1993 the deepest bore-hole through the Greenland Ice Cap was drilled at Summit by PICO in support of the GISP2 Project, Greenland Ice Sheet Program II (*Kelley et al*. 1994). Geophysical measurements carried out in 1995 showed that due to the inclined nature of the GISP2 bore-hole, the total GISP2 bore-hole length of 3056,4 m is 8,6 m longer than the true vertical depth (*Clow and Gundestrup*, 1999).

n-Butyl acetate was used as a drilling fluid. It is known that n-butyl acetate dissolves ice slightly. The water solubility in n-butyl acetate is 2,88 % by mass at temperature 25 °C and decreases at lower temperature (*Industrial Solvents Handbook*, 1991). A 20 g cube of ice lost in 1 hour 1 % of its mass in n-butyl acetate at –19 °C (*Gosink et al.*, 1991). That n-butyl acetate to some degree can dissolve ice is ignored in the following calculations.

In August of 1995 the GISP2 bore-hole logging with UCPH logger included the measurements of the temperature (temperature profile see *Table 4*) and the absolute pressure (at *Table 11* the measured absolute pressure is converted to hydrostatic pressure subtracting the atmospheric pressure of 0,066 MPa).

Table 11. Measured and calculated hydrostatic pressure [MPa] *in GISP2 bore-hole according to linear density-temperature relation of n-butyl acetate (the fluid top H_0 = 76,6 m)*

Depth, m	**Measured hydrostatic pressure (1995)**	**Calculated hydrostatic pressure based on temperature**	**Calculated hydrostatic pressure based on temperature and compressibility**
102,2	0,233	0,234	0,234
254,7	1,625	1,629	1,630
502,9	3,898	3,899	3,905
753,7	6,205	6,192	6,207
1003,8	8,504	8,480	8,508
1254,0	10,811	9,255	10,815
1503,4	13,118	13,051	13,119
1747,5	15,372	15.285	15,378
2001,8	17,727	17,210	17,733
2252,8	20,049	19,898	20,057
2500,5	22,332	22,147	22,345
2749,7	24,623	24,397	24,639
2999,0	26,903	26,633	26,926
3046,6	27,330	27,059	27,360

At the GISP2 site the acceleration of gravity increases with depth (*K.Keller*, personal communication):

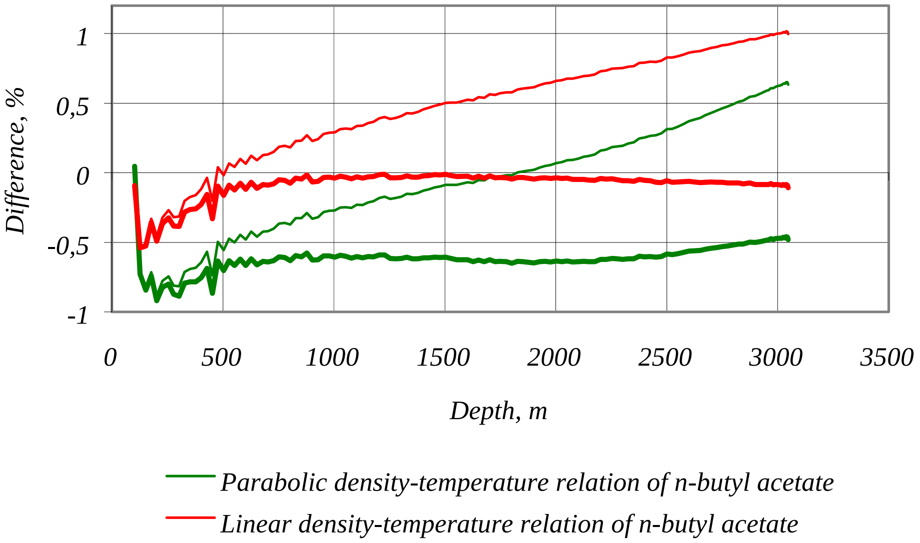
$$g = 9{,}817953 + 2{,}31467 \cdot 10^{-6} z. \quad (34)$$

According to equations (14) and (18) the hydrostatic pressure is calculated in 25 m steps using parabolic density-temperature relation of n-butyl acetate (see *Fig. 2* and *Table 3*). This was done for two cases: first is the hydrostatic pressure is corrected for temperature (*Fig. 2*, thin green line), second the hydrostatic pressure is corrected for temperature and compressibility (*Fig. 2*, thickened green line).

We see that the difference between measured and calculated pressure in both cases is rather high. In the second case, when compressibility is accounted for, the difference is nearly 0,6 % independent on depths, indicating that the compressibility is correct. Therefore, we decided to check density-temperature equation of n-butyl acetate. Experiments carried out in

Copenhagen University showed a linear density-temperature relation of n-butyl acetate at -57,6 °C < t < 22,4°C (see *Fig. 2* and *Table 3*).

Fig. 3. Difference between measured and calculated pressure (thin lines - based on temperature; thickened lines - based on temperature and compressibility)



Then the calculations were repeated (*Table 11*) and now the difference between measured and calculated pressure, based on temperature and compressibility, is less than 0,12 % in most of the bore-hole (*Fig.2*, thickened red line). At the bottom of the GISP2 bore-hole the difference is only 0,03 MPa. At the upper part of the GISP2 bore-hole the difference between measured and calculated pressure is about 0,5% probably because the fluid contains some amount of the ice chips.

The difference between the measured pressure and the pressure, based on temperature only, increases with depth and at the bottom of the bore-hole it achieves 0,27 MPa or 1%.

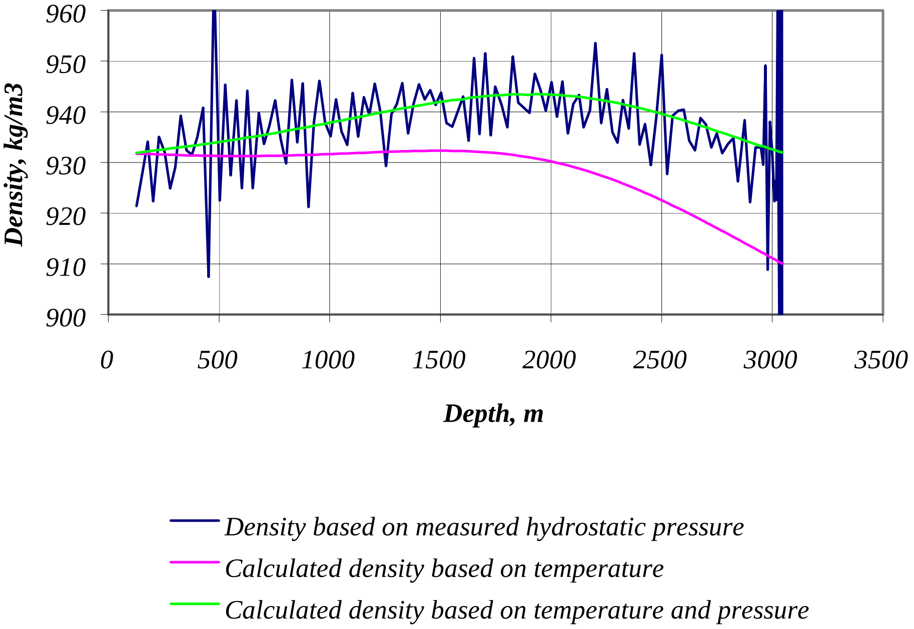
Measurements of hydrostatic pressure and vertical depth make it possible to calculate the average density of drilling fluid over given depths interval, but if the interval h_i is small, the average density at this interval is approximately equal to the real density at the depth z_i:

$$\rho_{fl}^{P,t}(z_i) \approx \frac{P_{fl}^{m}(z_i) - P_{fl}^{m}(z_{i-1})}{gh_i}, \tag{35}$$

where $P_{fl}^{m}(z_i)$ and $P_{fl}^{m}(z_{i-1})$ are measured hydrostatic pressure at the vertical depths z_i and z_{i-1}, respectively.

The fluid density in the GISP2 bore-hole is estimated according to equation (35) with $h_i \approx 25$ m (*Fig.4*). The curve has parabolic shape with high frequency errors in the order of 5-10 kg/m^3 due to the limited resolution of the pressure sensor. The theoretical density profiles in the GISP2 bore-hole are also shown. The calculated density profile based on temperature and pressure is in a good agreement with the bore-hole measurements.

Fig.4. Density profile in GISP2 bore-hole



Density of n-butyl acetate in GISP2 bore-hole smoothly increases from 931,7 kg/m^3 at the fluid top to 943,4 kg/m^3 at the depth of 2000 m. Then it is decreased to 932,0 kg/m^3 at the bottom of the bore-hole.

The very high correlation between measured hydrostatic pressure and calculated pressure corrected for thermal expansion and compressibility of the fluid confirms the foregoing method. For GISP2, the ice pressure at the bottom of the hole is estimated to 27,30 MPa compared to 27,36 MPa calculated and 27,33 MPa measured bore-hole pressure. Therefore, the GISP2 bore-hole is close to the pressure equilibrium.

Pressure difference and choice of the fluid density

At the beginning of this chapter we noticed that the choice of the fluid density is connected with the estimation of pressure difference between fluid and ice. The stability of the bore-hole is ensured when hydrostatic pressure of fluid is equal to overburden pressure of ice: $\Delta P(z) = 0$.

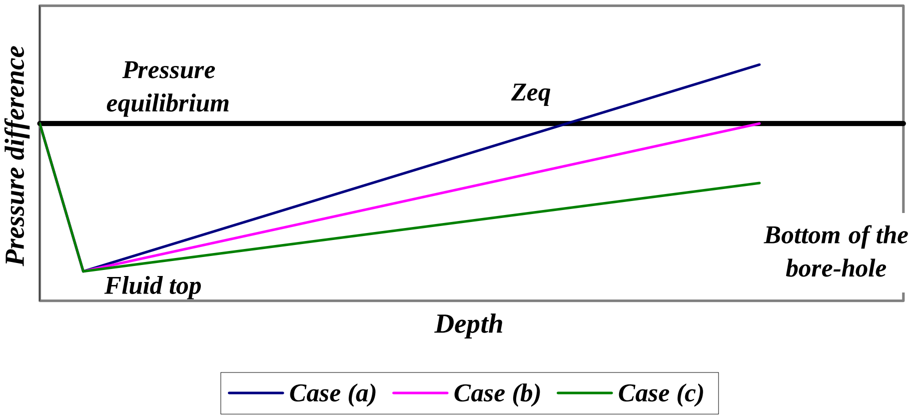
In practice the pressure equilibrium can’t be achieved at the entire bore-hole. There are three main cases of the pressure difference profile in bore-hole (these cases are schematically shown at *Fig. 5*):

(a) at the upper part of the bore-hole the pressure difference is negative and at the lower part it is positive (pressure equilibrium exists at the depth z_{eq});

(b) the pressure equilibrium exists near the bottom of the bore-hole and at the upper part of the bore-hole the pressure difference is negative;

(c) at the entire bore-hole the pressure difference is negative.

Fig. 5. Pressure difference profiles in bore-hole



The practice of ice coring showed that drilling is possible even in the case of the insignificant negative pressure difference. The maximal threshold for the pressure difference depends on the ice temperature, orientation and size of ice crystals, impurities and other factors (the regularities of the bore-hole closure are described in the next Chapter “*Bore-hole closure rate*”). If the pressure difference is too high the bore-hole will deform and prevent the further drilling.

The main factor of the bore-hole closure rate is the temperature of ice. The upper parts of the Antarctic and Greenland ice caps have extremely low temperatures, and the rate of the bore-hole closure in the condition of non-full compensated pressure is slow. For example, at Vostok Station (Central Antarctica) the pressure difference of 0,8-1,0 MPa at the depths above 2000 m causes the hole closure of about 0,1 – 0,2 mm/a only (*Tchistiakov et al.*, 1994). At the deeper depths the rate of bore-hole closure increases significantly (*Table 12*).

Table 12. The rate [*mm/a*] *of the bore-hole closure at Vostok Station (according to equations of Tchistiakov et al.*, 1994*)*

Pressure difference, MPa	**Depth, m**			
	2250	**2500**	**2750**	**3000**
0,5	0,1	0,2	0,4	0,7
1,0	0,8	1,5	2,7	5,3
1,5	2,7	5,0	9,3	18,0
2,0	6,5	11,8	22,0	42,5
2,5	12,8	23,0	42,9	83,1
3,0	22,1	39,7	74,1	143,5

So, to estimate the necessary fluid density, at first, the depth z_{eq} of the pressure equilibrium have to be chosen (recommended depth z_{eq} is about 2500 m for Central Antarctica and about 2000 m for Central Greenland; from these depths the internal temperature of ice increases very fast).

For pressure equilibrium at the depth z_{eq} equations (2) and (18) lead to the main criteria for the choice of the fluid density:

$$\int_{H_0}^{z_{eq}} \rho_{fl}(z)dz = \overline{\rho}_{ice}(z - H_1)\,. \tag{36}$$

Solving of this equation is possible by the method of consecutive approximation. But this way is inconvenient because the result density include thermal expansion and compressibility and, therefore, its value will be rather different from the density that we have at the surface.

For the preliminary choice of the fluid we recommend, at first, to use the average value of fluid density in bore-hole (from depth H_0 to z_{eq}):

$$\overline{\rho}_{fl} = \frac{\int \rho_{fl}(z)dz}{z_{eq} - H_0}\,, \tag{37}$$

or

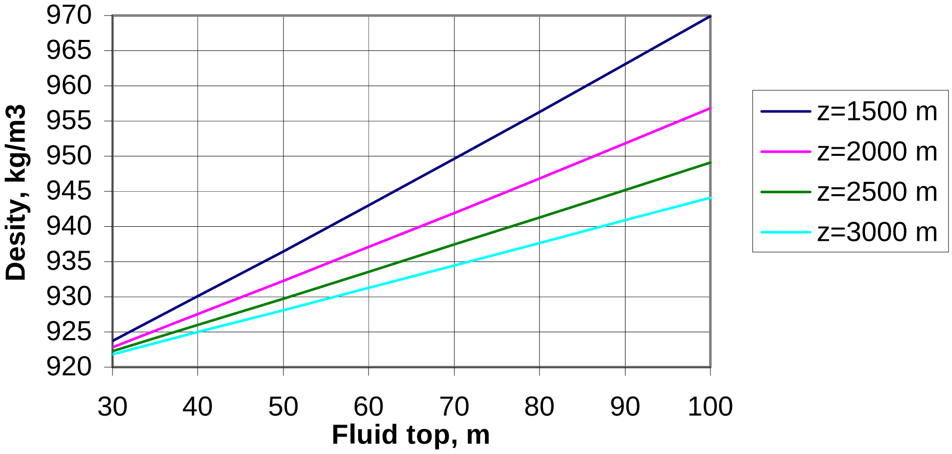
$$\overline{\rho}_{fl} = \frac{\sum \rho_{fl}^{P,t}(z_{i-1})h_i}{z_{eq} - H_0}. \tag{38}$$

Thus, the pressure equilibrium at the depth z_{eq} should be at the following average density of fluid:

$$\overline{\rho}_{fl} = \overline{\rho}_{ice}\frac{z_{eq} - H_1}{z_{eq} - H_0}. \tag{39}$$

If the fluid top is situated at the depth of 60 m, the average density needed for the full compensation of ice-overburden pressure is about 943 kg/m^3 at the depth 1500 m and 931,2 kg/m^3 at the depth 3000 m (*Fig. 6*).

Fig. 6. Average density of fluid needed for pressure equilibrium versus fluid top (average density of ice 920 kg/m3; firn correction 24 m)



To exclude the influence of pressure on the fluid density, at the first stage the average density of the fluid can be approximately found according to:

$$\overline{\rho}_{fl}^{t} = \frac{1}{k_c}\overline{\rho}_{fl}, \tag{40}$$

where k_c is the empirical coefficient accounting the fluid compressibility (for the depths 2000 – 3000 m in cold glaciers coefficient k_c is about 1,01).

Finally, the average density of the fluid $\overline{\rho}_{fl}^{t}$ in the bore-hole may be estimated as the density at the average temperature in the bore-hole (from depth H_0 to z):

$$\bar{t} = \frac{1}{z - H_0} \int t(z) dz \, , \tag{41}$$

where $t(z)$ is the temperature profile in the bore-hole.

Summarizing these considerations, the choice of the fluid density includes following:

1. At first, the fluid top H_0 is chosen due to the technological and environmental requests.
2. Then the depth z_{eq} of pressure equilibrium is chosen.
3. The average density of fluid in bore-hole $\bar{\rho}_{fl}$ needed for compensation of the overburden pressure at the depth z_{eq} is found according to equation (39).
4. The approximate fluid density under atmospheric pressure $\bar{\rho}_{fl}^{t}$ is calculated according to equation (43).
5. The average temperature $\bar{t}$ in bore-hole is determined according to (41) due to intended temperature profile in bore-hole.
6. The fluid is chosen: its density at average temperature in bore-hole should be approximately equal to the density $\bar{\rho}_{fl}^{t}$.
7. For two-compound fluid the concentration of densifier is calculated according to equation (24).
8. The difference between the hydrostatic pressure of fluid and the overburden pressure of ice is estimated from surface to the final depth according to equations (4a), (9) and (18).
9. In all cases of negative pressure difference the rate of the hole closure should be estimated (see Chapter “*Bore-hole closure rate*”).
10. If the rate of bore-hole closure is too high the chosen fluid density should be increased, and the prognosis of the bore-hole closure rate is repeated.
11. The correctness of the chosen fluid density is checked *in situ* using pressure measurements in bore-hole.

The foregoing method allows to choose the correct fluid density for the concrete drilling site. This method is suitable both for one and two-compound fluids. To estimate the pressure difference between fluid and ice it is necessary to know: (a) intended temperature profile in bore-hole; (b) density-temperature relation of drilling fluid; (c) compressibility of drilling fluid; (d) intended density profile of ice (or average density of ice and depth of firn correction).

Choice of the fluid density for 3000-m bore-hole at Central Greenland

We illustrate method of the fluid density choice on example of the Drilling Project at Camp North GRIP (Central Greenland) in 1999-2000.

1. The experience of the ice deep drilling at Summit in 1990-1992 (*Gundestrup et al.,* 1994b) and Camp NGRIP in 1996-1997 (*Gundestrup*, 1996 and 1997) showed that the fluid top H_0 near 60 m below the surface is satisfactory for technological and environmental requests.

2. Firn correction at Central Greenland is 24 m (*Gundestrup et al*., 1994b). The most rapid rates of bore-hole closure are at depths below 2000 m (*Clow and Gundestrup*, 1999). Therefore, the depth z_{eq} of pressure equilibrium should be about 2000 m.

3. The average density of ice in Central Greenland can be taken as 920 kg/m^3 (*Gundestrup et al*., 1994). The average density $\bar{\rho}_{fl}$, needed for the compensation of ice pressure at the depth z_{eq} = 2000 m according to equation (39), is 937 kg/m^3.

4. The approximate fluid density $\bar{\rho}_{fl}^{\,t}$ under atmospheric pressure is 928 kg/m^3 (coefficient $k_c = 1{,}01$).

5. The average temperature $\bar{t}$ [°C] in the interval of 60 – z m is determined according to temperature profile for Camp GRIP (*Table 4*) and equation (41):

$$\bar{t} = -31{,}69 + 1{,}322\cdot10^{-3}z - 1{,}891\cdot10^{-6}z^2 + 6{,}311\cdot10^{-10}z^3 .$$

Average temperature $\bar{t}$ in the interval of 60 – 2000 m is –31,5 °C.

6. We choose the following two potential drilling fluids:

a) mixture of Exxol D60 and densifier HCFC 123 with density 928 kg/m^3 at – 31,5 °C;

b) silicon oil KF96-2,0cs with density 925 kg/m^3 at –31,5 °C.

7. To prepare the mixture with chosen density, the mass concentration C_M of densifier HCFC 123 is 0,235. Traditionally drilling fluid for sites in Central Greenland has density 935 kg/m^3 at –30 °C. It means that the mass concentration of densifier HCFC 123 in mixture with Exxol D60 should be equal to 0,25.

8. The real density profile (*Fig.7*) based on temperature and pressure for mixture of Exxol D60 and HCFC 123 with densifier concentration of 0,235 and 0,25, as well as, for silicon oil KF96-2,0cs is estimated according to equations of *Table 6.*

Then the difference between hydrostatic and overburden pressure is estimated from the surface to the bottom of 3000-m bore-hole (*Fig. 8*).

Fig.7. Density profiles of potential drilling fluids in 3000-m bore-hole at Central Greenland

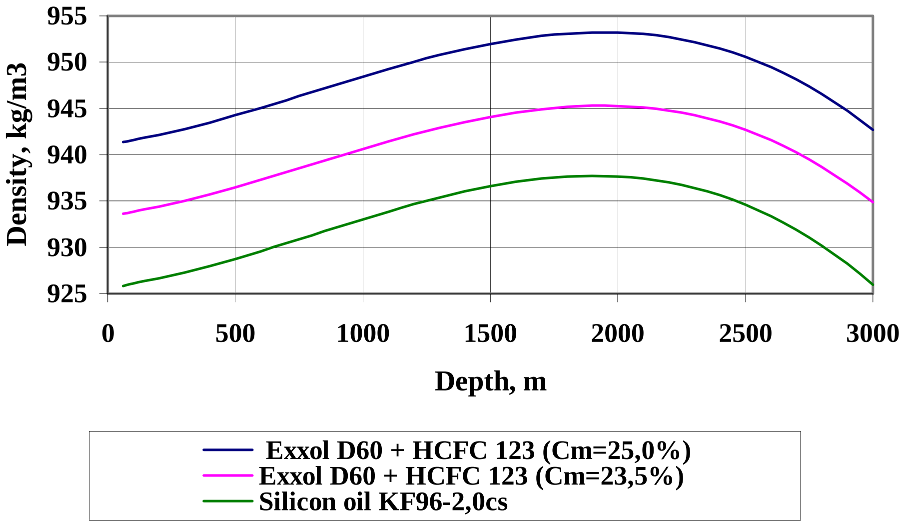
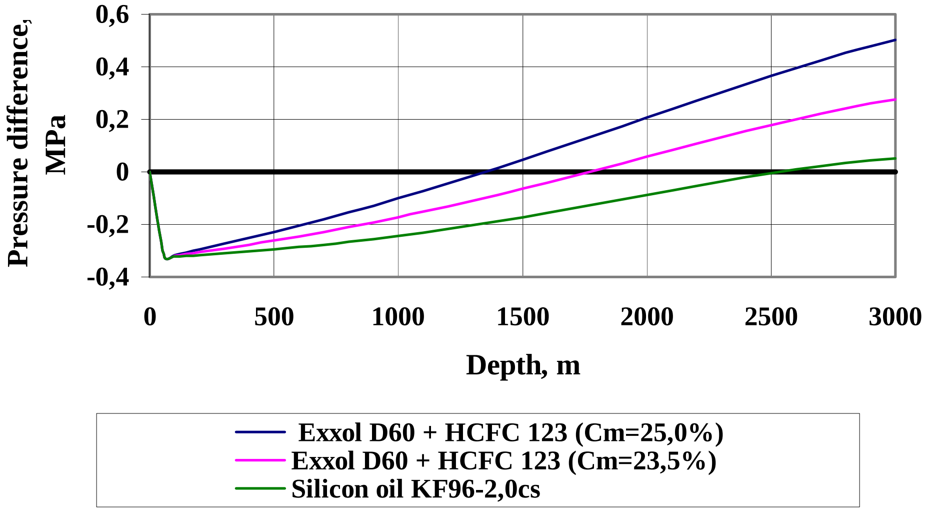


Fig.8. Difference between hydrostatic pressure and overburden pressure in 3000-m bore-hole (fluid top at 60 m)



The pressure equilibrium z_{eq} is at the depth of 1350 m for mixture of Exxol D60 + 25,0 % HCFC 123, at the depth of 1730 m for mixture of Exxol D60 + 23,5 % HCFC 123 and at the depth of 2560 m for silicone oil. In all three cases the negative pressure difference more than 0,1 MPa happens at the depths above 2000 m, where the ice has the lower temperatures and the rate of the bore-hole closure will be slow. Prognosis of the bore-hole closure for the most unfavorable case (silicon oil KF96-2,0cs) is in the next chapter.

3. BORE-HOLE CLOSURE RATE

Bore hole closure and drilling technology

One of the main ideas of ice deep drilling technology is the limitation of the closure rate due to the control density of drilling fluid. It is impossible to prevent bore-hole at all because anyway there are parts in the bore-hole where the ice pressure is more than pressure of fluid (see *Fig. 5* on page 31). Therefore, the choice of the fluid density is directly connected with the estimation of the bore-hole closure rate. The maximal value of the hole diameter changing is fixed according with the kind of ice drilling and proposed drilling time.

The thermal drilling is characterized by the law mechanical penetration rate and the high hole enlarging during drilling. The coefficient of diameter enlarging is about 1,05-1,08 (it means that diameter of the bore-hole is in 1,05-1,08 times higher than the diameter of drill head). The diameter of the bore-hole drilled by electromechanical drills is near the diameter of the drill head, and the coefficient of enlarging is 1,002-1,02 only.

The maximal value of the hole diameter changing, that guaranteed drilling process without sticking, is

$$\Delta D = bd_h(k_e - 1), \tag{1}$$

where d_h is the outer diameter of the drill head, m; k_e is the proposed coefficient of enlarging, b is the safe coefficient accounting the bore-hole bending, non-roundness of bore-hole section and other factors (b = 0,5 - 0,7).

Then the minimal safe diameter can be calculated:

$$D_{\min} = D_0 - \Delta D\,, \tag{2a}$$

or

$$D_{\min} = d_h\left[k_e(1-b) + b\right]\,, \tag{2b}$$

where D_0 is the initial diameter of bore-hole, m.

The time [h] of drilling from the depth z_0 up to the depth z can be estimated according to:

$$T(z) = \frac{(z-z_0)z}{3600lv_l} + \frac{z-z_0}{l}T_s + \frac{z-z_0}{v_m} + T^*, \tag{3}$$

where l is the penetration for one run, m; v_l is the average rate of lowering/hoisting of the drill, m/s; T_s is the time of the drill servicing between runs, h; v_m is the mechanical rate of penetration, m/h; T^* is the unproductive time (cleaning of the hole, bore-hole measurements, standing idle and so on), h.

Usually unproductive time is accounting by the coefficient k_u (*Table 1*):

$$T(z) = k_u \left[\frac{(z - z_0)z}{3600 l v_l} + \frac{z - z_0}{l} T_s + \frac{z - z_0}{v_m} \right]. \tag{4}$$

Table 1. The estimation of coefficient k_u

Drilling site	**Interval, m**		***l*, m**	**v_l, m/s**	**v_m, m/h**	**T_s, h**	**Theoretical rate*, m/week**	**Practical rate, m/week**	**k_u**
	z_0	**z**							
NGRIP96	115	351	3,4	1	10,1	0,3	703,4	91,8	7,66
NGRIP97	351	1371	3,4	1	10,1	0,3	650,8	134,7	4,83

*Theoretical rate is calculated at $k_u = 1$.

The time of the bore-hole standing at the depth z is

$$\Delta T(z) = T(H) - T(z), \tag{5}$$

where $T(H)$ is the total time of drilling up to the final depth H, h.

The influence of the destruction process during drilling to the hole closure rate isn't clear. The thermal destruction is accompanied by thermal blow at the bottom of the hole, and the recrystallization process near the bore-hole wall is observed. During electromechanical drilling in a contradistinction to thermal drilling ice crystals are cutting, and molecular links are destroying. We don't have experimental data concerning the influence of the destruction process to the rate of the hole closure.

Until more data are available, it seems to use equation (2b) in any kind of ice destruction.

Ice creep

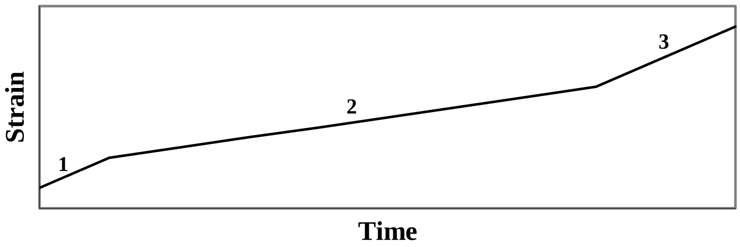
The ice deformation depends mainly on the rate of loading and temperature. Due to the continual increasing of the loading rate ice works consecutively as elastic, plastic and brittle material.

The dynamics theory of the large ice masses accepts the ice as a perfectly plastic material and considers the following kinds of ice deformations (*Fig. 1*):

1) first-order (primary or transient) creep;
2) secondary (steady or *Glen*-type) creep;
3) tertiary (recrystallization) creep.

An initial elastic deformation is followed by a period of first-order ice creep, in which the stain rate decreases continuously. The subsequent decelerations produce strain-rate minimum that approach secondary creep. Further accelerations produce maximum strain-rates that are assumed to approach tertiary creep.

Fig. 1. Ice creep curve



Three stages of ice creep were confirmed by many years bore-hole measurements in the Devon Island Ice Cap (*Paterson*, 1977), Agassiz Cap (*Fisher and Koerner*, 1986) and at Vostok Station, Antarctica (*Blinov and Dmitriev*, 1987).

The deformation of ice near the bore-hole is shown at *Fig. 2*. According to plastic theory (*Nye*, 1953) the normal-stress components on the walls of the cylindrical bore-hole are:

$$\sigma_\theta = -\frac{2p}{n}; \quad \sigma_z = -\frac{p}{n}; \quad \tau = \frac{p}{n}, \tag{6}$$

where p is the pressure; n is the parameter.

Generally, the shear strain rate of ice $\dot{\varepsilon}_r$ is connected with shear stress τ as

$$\dot{\varepsilon}_r = A\tau^n, \tag{7}$$

where A is the flow parameter.

Numerous laboratory experiments and field data confirmed this equation, usually called as *Glen's* Law. Empirical values of A and n are widely different. Measuring of bore-hole closure gave the following view of *Glen's* Law for the secondary creep ($\dot{\varepsilon}$ in [s^{-1}] and τ in [MPa]):

$\dot{\varepsilon}_r = 1{,}54\times10^{-8}\tau^3$ at –22 °C (*Paterson*, 1977); (8)

$\dot{\varepsilon}_r = 1{,}27\times10^{-8}\tau^{2{,}7}$ at –22 °C (*Fisher and Koerner*, 1986); (9)

$\dot{\varepsilon}_r = 6{,}49\times10^{-9}\tau^{2{,}87}$ at –35 °C (*Naruse et al.*, 1988); (10)

$\dot{\varepsilon}_r = 4{,}85\times10^{-10}\tau^{3{,}5}$ at –53 °C (*Blinov and Dmitriev*, 1987). (11)

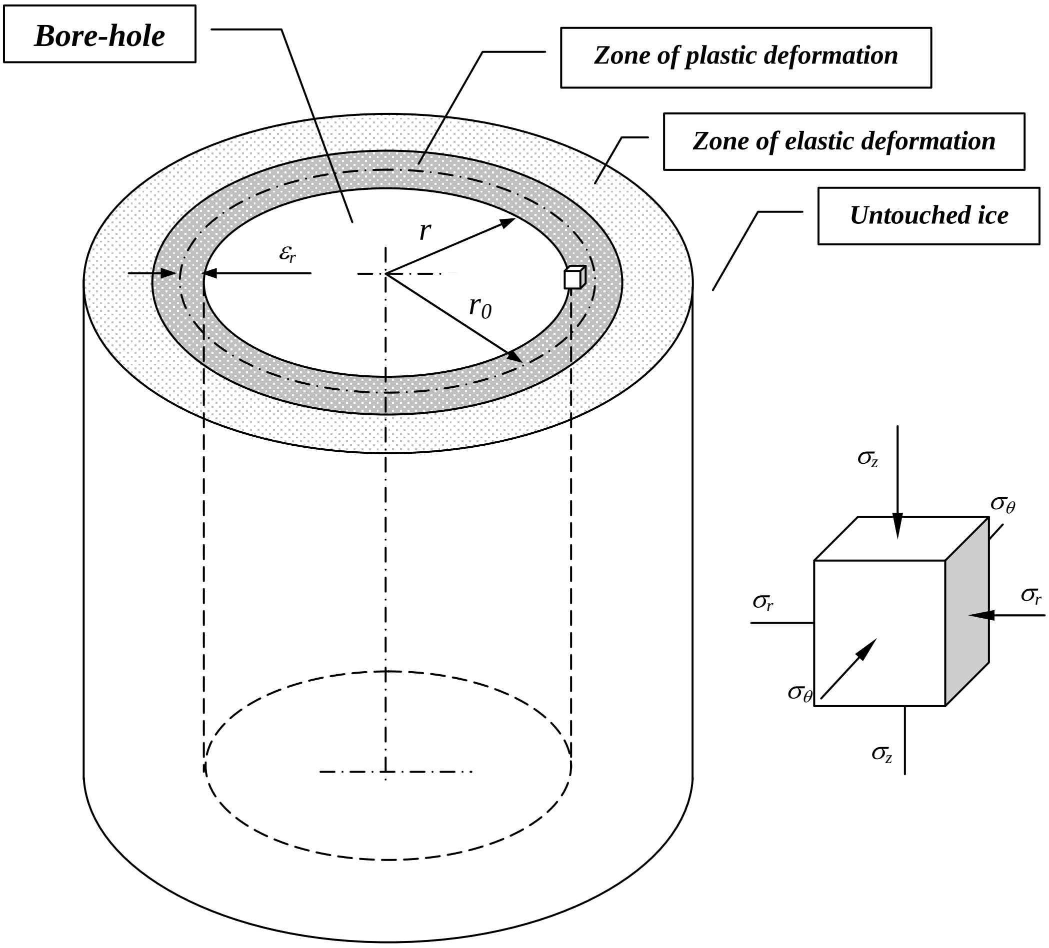


Fig. 2. Deformation of ice near the bore-hole (r_0 – initial radius; r – current radius)

There are no the universally recognized method for the estimation of flow parameter *A* and power *n.* The *Paterson's* (1994) recommendations are the most widespread, but they have disadvantages discussed below.

For a Newtonian substances, when the rate of deformation and stress are proportional, the power $n = 1$, and equation (7) leads to

$$\dot{\varepsilon}_r = A\tau, \tag{12}$$

or

$$\dot{\varepsilon}_r = \frac{\sigma_a}{2\eta}, \tag{13}$$

where σ_a the is elastic limit; η is the coefficient of viscosity.

Unlike Newtonian viscous materials the ice coefficient of viscosity varies with the stress. Values of ice coefficient of viscosity varied from 10^8 to 10^{14} Pa·s (*Hobbs*, 1974), which indicated that ice is not a Newtonian material.

Flow parameter *A*

The flow parameter *A* depends on ice temperature, crystal orientation, dust content and other factors. To separate effect of temperature from other factors, the flow parameter *A* is dividing as

$$A = kA(t)\,, \tag{14}$$

where $A(t)$ is the flow parameter, varying with temperature only; k is the enhancement coefficient, accounting orientation and size of ice crystals, texture, fabric, impurities and other factors.

The influence of temperature on the flow parameter $A(t)$ [$\mathrm{Pa^{-3}\cdot a^{-1}}$] usually is interpreted according to *Arrenius* function:

$$A(t) = A_0 \exp\left(-\frac{Q}{Rt_K}\right), \tag{15}$$

where A_0 is the constant parameter independent on temperature, $\mathrm{Pa^{-3}\cdot a^{-1}}$; Q is the activation energy of creep, J/mol; R is the universal gas constant (R = 8,314 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$); t_K is the absolute temperature, K.

The value of creep activation energy Q varies too. According to results of creep experiments *Fletcher* (1970) obtained the activation energy of 59,7 ± 5,7 kJ/mol. *Hobbs* (1974) recommended to use Q = 54,9 kJ/mol. Preliminarily *Paterson* (1977) recommended to use Q=54 kJ/mol, but then he changed this recommendation.

At temperatures below –10 °C *Paterson* (1994) used the mean creep energy activation Q=60 kJ/mol, and he noted that value of activation energy depends on temperature. At temperatures between 0 and –10 °C energy activation Q increases up to 139 kJ/mol, and *Arrenius* function in equation (15) doesn't work. Therefore, at these temperatures *Paterson* (1994) used mean values of $A(t)$ measured by tests.

In references there are many recommendations for the choice of the constant parameter A_0. At Q=54 kJ/mol *Paterson* (1977) used A_0=8,4·10^{-8} $\mathrm{Pa^{-3}\cdot a^{-1}}$. At Q=60 kJ/mol *Dahl-*

*Jensen (*1985) used A_0=9,8·10^{-6} $Pa^{-3}\cdot a^{-1}$, *Dahl-Jensen and Gundestrup* (1987) A_0=2,23·10^{-5} $Pa^{-3}\cdot a^{-1}$, *Clow and Gundestrup* (1998) A_0=1,26·10^{-5} $Pa^{-3}\cdot a^{-1}$. In *Table 2* the results of A_0 estimation according to *Paterson's* (1994) recommendations are represented.

Table 2. Recommended values of flow parameter A(t) at n=3 (Paterson, 1994*), Arrenius function (Q=60 kJ/mol) and calculated constant parameter A_0 at different temperatures*

t, °C	*A (t)*		$\exp\left(-\frac{Q}{Rt_K}\right)$	A_0	
	$kPa^{-3}\cdot s^{-1}$	$Pa^{-3}\cdot a^{-1}$		$kPa^{-3}\cdot s^{-1}$	$Pa^{-3}\cdot a^{-1}$
0	$6,8\cdot 10^{-15}$	$2,1\cdot 10^{-16}$	-	-	-
-2	2,4	$7,5\cdot 10^{-17}$	-	-	-
-5	1,6	5,0	-	-	-
-10	$4,9\cdot 10^{-16}$	1,5	$1,224\cdot 10^{-12}$	$4,00\cdot 10^{-4}$	$1,26\cdot 10^{-5}$
-15	2,9	$9,1\cdot 10^{-18}$	$7,196\cdot 10^{-13}$	4,02	1,27
-20	1,7	5,4	4,142	4,10	1,29
-25	$9,4\cdot 10^{-17}$	2,9	2,331	4,03	1,27
-30	5,1	1,6	1,282	3,98	1,25
-35	2,7	1,1	$6,873\cdot 10^{-14}$	3,92	1,24
-40	1,4	$4,4\cdot 10^{-19}$	3,587	3,90	1,23
-45	$7,3\cdot 10^{-18}$	2,3	1,820	4,01	1,26
-50	3,6	1,1	$8,956\cdot 10^{-15}$	4,02	1,26

We see that the temperature has a complicated influence on the value of the creep energy activation *Q*, and the choice of the constant parameter A_0 isn't simple too. Furthermore, *Mellor and Smith* (1967) pointed out a disparity of *Arrenius* function to the natural ice temperatures and suggested to use following empirical relation:

$$A(t) = A_0^{\ *} e^{at}, \tag{16}$$

where A_0^* is the constant parameter, $Pa^{-3}\cdot a^{-1}$; *a* is the empirical coefficient, $°C^{-1}$; *t* is the temperature, °C.

Different experiments have obtained values of the coefficient *a* in equation (16) from 0,091 to 0,111 (*Budd*, 1969). The interpretation of *Paterson's* (1994) recommendation gives the following equation [$Pa^{-3}\cdot a^{-1}$]:

$$A(t) = 6 \times 10^{-17} e^{0,12t}. \tag{17}$$

Enhancement coefficient

The main disadvantage of ice creep theory is the absence of exact recommendations for the estimation of the enhancement coefficient k in equation (14). Originally the flow parameter was equated to $A(t)$. But the bore-hole measurements *in situ* showed that experimental values of the flow parameter is significantly higher than $A(t)$ (*Russel-Head and Budd*, 1979).

The measurements of bore-hole tilting in Dye 3 bore-hole, Greenland (*Dahl-Jensen and Gundestrup*, 1987) showed that in Holocene ice the enhancement coefficient k is equal to 1. At the boundary between Holocene and Wisconsin ice (the depth of about 1800 m) the enhancement coefficient rapidly increased up to 3,0-3,7 and then slowly decreased to 1,8-2,0 at the depth of 2000 m. Then the second maximum of enhancement coefficient (k ~ 3,4) was observed in 25-m zone of silty ice at the bottom of the bore-hole.

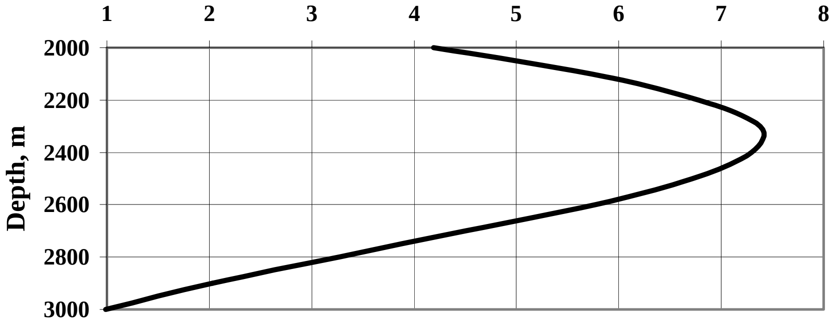
Similar increases of the coefficient k were observed at the boundary Holocene - Wisconsin in bore-holes at Camp Century, Greenland, and Byrd Station in Antarctica (*Gundestrup et al*., 1993). *Dahl-Jensen and Gundestrup* (1987) suggested that high deformation rate in Wisconsin ice is due to the high impurity contents and/or the small crystal size.

This conclusion was confirmed by measurements of bore-hole closure at Agassiz Ice Cap (*Fisher and Koerner*, 1987), where the strain-rates of Holocene ice fit to the term $k = 1$. But the older ice close significantly faster having closure strain-rates nearly three times the Holocene values.

Paterson (1994) had discussed possible explanations for the softness of the Wisconsin ice too. He concluded that the cause of the enhanced deformation is the abrupt transformation of the fabric to a strong single maximum, observed to occur across the Holocene – Wisconsin transition.

The measurements of bore-hole tilting in GISP2 bore-hole, Greenland (*Clow and Gundestrup*, 1999), showed another profile of enhancement coefficient (*Fig.3*). In contradiction to the data of Dye 3 and Camp Century the enhancement coefficient doesn’t leap at the boundary of Holocene – Wisconsin (for GISP2 bore-hole this boundary is at the depth of about 1600 m). The enhancement coefficient smoothly increases to a maximum value of 7-9 at the depth of 2300-2400 m. Authors suggested that this high values is associated with dusty fine-grained Wisconsin ice.

Fig.3. Enhancement coefficient k, calculated for GISP2 bore-hole (Clow and Gundestrup, 1999)



Below 2400 m *k* progressively declines to a value of 1,0 – 1,5 above the basal ice zone. This section generally continues to be dusty and fine grained, and the reduction of coefficient *k Clow and Gundestrup* connected with increased incidence of layer waviness, inclined layers, folding, and "crystal striping". Within the basal ice zone (vertical depth 3033-3048 m) the enhancement coefficient jumps back up to 5-8.

The interpretation of data from *Fig.3* gives the following relation of the enhancement coefficient *k versus* vertical depth *z* [m] in GISP2 bore-hole at the interval 2000-3000 m assuming $A_0 = 1{,}26 \cdot 10^{-5}\ \mathrm{Pa}^{-3} \cdot \mathrm{a}^{-1}$:

$$k = 1{,}76 \times 10^{-8} z^3 - 1{,}49 \times 10^{-4} z^2 + 0{,}406 z - 354\,. \tag{18}$$

At Vostok Station, Antarctica, the diameter measurements of the bore-hole 3G made in 1986 and 1990 showed that the measured flow parameter is lower than *Paterson's* (1994) parameter $A(t)$ in 1,5-2 times (*K.V.Blinov*, personal communication). In that case we can call the coefficient *k* as "reduction coefficient". The reduction of the deformation rate possibly is connected with special properties of ice in Central Antarctica.

Glen's Law power *n*

The value of power *n* in *Glen's* Law (7) should be a constant, but it varies from 1,5 to 4,2 for the different types of glaciers and glacier layers (*Paterson*, 1994).

At GISP2 bore-hole mean value of the power *n* is assumed to be between 2 and 3 (*Dahl-Jensen and Gundestrup,* 1987); at Mizuho Station, Antarctica, the power *n* is little less than 3 (*Naruse et al*, 1988); at Vostok Station, Antarctica, n = 3,5 (*Blinov and Dmitriev*, 1987).

Hobbs (1974) considered that between –2 and –45 °C the value of power n is essentially constant at about 3. *Paterson* (1994) also recommended using n = 3 in ice sheet-modelling until more data are available.

Glen's Law and the rate of the bore-hole closure

Foregoing considerations show that the flow parameter A and power n in *Glen's* Law (7) can be exactly determined only for the concrete drilling site by experimental measurements. Nevertheless, we can evaluate the hole closure rate using *Paterson's* recommendations and approximate value of enhancement coefficient k.

The theory of the hole closure in isotropic ice, as given by *Nye* (1953) and then used by *Paterson* (1977), is followed here. Shear strain rate is a function from time T :

$$\dot{\varepsilon}_r = \frac{dr}{r_0 dT}, \tag{19}$$

where r and r_0 are current and initial radiuses of the bore-hole (see *Fig. 2*).

Equating (19) and (7), we have

$$\frac{dr}{r_0 dT} = A\tau^n, \tag{20}$$

or

$$\frac{dr}{r_0} = A\tau^n dT. \tag{21}$$

Equation (6) for the shear stress at the walls of the cylindrical hole gives at $p = \Delta P(z)$:

$$\tau = \frac{\Delta P(z)}{n}, \tag{22}$$

where $\Delta P(z)$ is pressure difference between fluid and ice: $\Delta P(z) = P_{fl}(z) - P_{ice}(z)$.

Substitution for τ in equation (21) leads to

$$\frac{dr}{r_0} = A\left(\frac{\Delta P(z)}{n}\right)^n dT, \tag{23}$$

After integrating and solving of this equation, the new radius r of the bore-hole after the time ΔT should be (*Pashkevich and Chistyakov*, 1989):

$$r = r_0 \exp\left[A \left(\frac{\Delta P(z)}{n} \right)^n \Delta T \right]. \tag{24}$$

Similar reasoning we see in the paper of *Tchistyakov et al*. (1994), but authors took $\dot{\varepsilon} = (r - r_0)/(r_0 T)$ instead of differential form, represented by equation (19).

Taking into account equations (14) and (17) at $n = 3$, we have:

$$r = r_0 \exp\left[2{,}2 \times 10^{-18} k e^{0{,}12t} \Delta P(z)^3 \Delta T \right], \tag{25a}$$

or

$$D = D_0 \exp\left[2{,}2 \times 10^{-18} k e^{0{,}12t} \Delta P^3 \Delta T \right], \tag{25b}$$

where r, r_0, D and D_0 in [m]; t in [°C]; $\Delta P(z)$ in [Pa]; ΔT in [years].

Finally, for the drilling up to the depth H and ensuring of the permissible hole closure the necessary average density of the drilling fluid can be estimated according to the following formula:

$$\bar{\rho}_{fl} = \frac{\bar{\rho}_{ice} g (H - H_1) + \left[\dfrac{\ln\left(1 - \Delta D / D_0\right)}{2{,}2 \times 10^{-18} k e^{0{,}12t} \Delta T} \right]^{1/3}}{g (H - H_0)} . \tag{26}$$

where $\bar{\rho}_{ice}$ is the average density of ice, kg/m^3; H_0 is the fluid top, m; H_1 is the firn correction, m. The permissible hole closure ΔD is determined according to equation (1), and the time of the bore-hole standing ΔT according to equation (5).

Prognosis of the bore-hole closure

The prognosis of the bore-hole closure is carried out for Drilling Project at Camp NGRIP (Central Greenland) in 1999 - 2000. We guess that drilling is conducted during two summer seasons: at first season up to the depth 1500 m and at the second season up to the depth 3000 m.

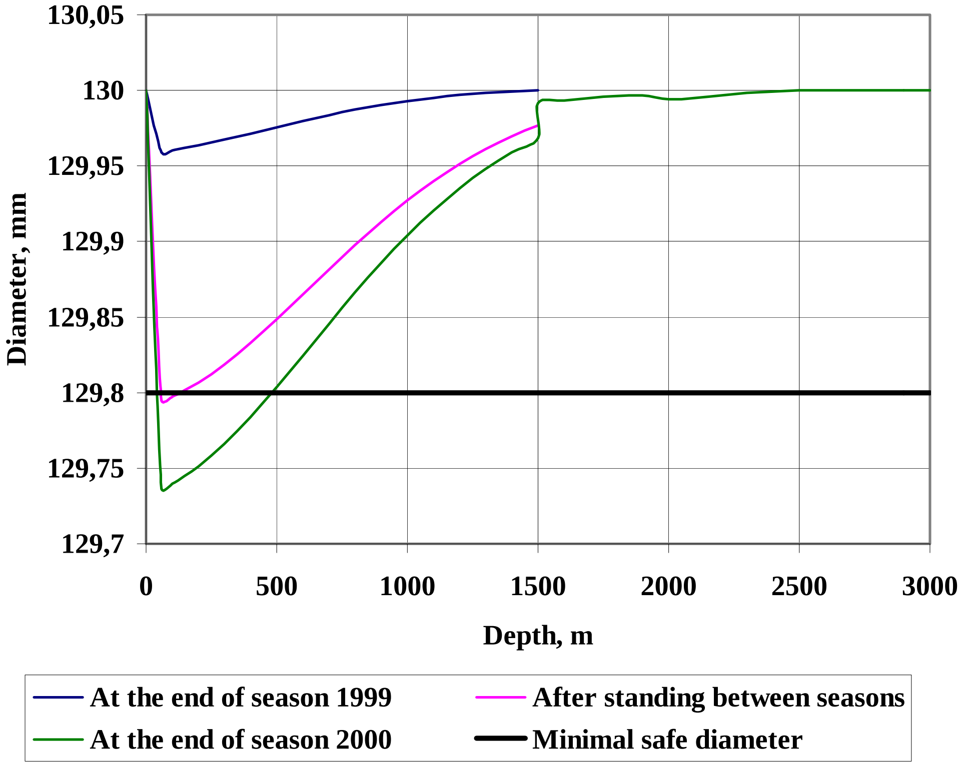
The temperature profile at North GRIP is approximated by the temperature at Camp GRIP (see *Table 4* on page 20). The enhancement coefficient k is taken equal 1,0 in the interval 0-1800, and it is calculated according to equation (18) in the interval 1800-3000 m.

The diameter of drill head d_h is 129,6 mm. Proposed coefficient of the bore-hole enlarging k_e of 1,003 gives the initial diameter of the bore-hole D_0 equal to 130 mm. Minimal safe diameter D_{min} according to equation (2b) at b = 0,5 is 129,8 mm.

The drilling fluid is silicon oil KF96-2,0cs, the fluid top is situated at the depth of 60 m supposedly. The difference between hydrostatic and overburden pressure was calculated in previous Chapter (see *Fig. 8* on page 36).

Then the changing diameter (*Fig. 4*) is calculated according to equation (25b).

Fig.4. Prognosis of the bore-hole diameter at North GRIP (drilling fluid - silicon oil KF96-2,0cs)



The analyze of curves at *Fig.4* gives:

1) Closure of the bore-hole during first season is in normal ranges.
2) At the second season drilling can be started after reaming of the upper part.
3) Pressure difference between fluid and ice at the Wisconsin ice is small (in the range from –0,1 to 0 MPa) due to the compressibility of the fluid, and the change of the bore-hole diameter during the second season doesn’t exceed 0,01 mm.

4. VISCOSITY

General considerations

The viscosity defines the property of fluids to offer the resistance to flow between different layers of fluid. In a Newtonian fluids the stress is directly proportional to the velocity gradient:

$$\tau = \eta \frac{\partial u}{\partial y}, \qquad (1)$$

where τ is the force per unit area; η is the coefficient of viscosity.

So, the property of internal friction of fluid is characterized by the *coefficient of viscosity* η (*coefficient of dynamic viscosity* or just *viscosity*). The *kinematic viscosity* ν is used in the modifying equations of motion of a perfect fluid to include the terms due to a real fluid:

$$\nu = \frac{\eta}{\rho_{fl}}, \qquad (2)$$

where ρ_{fl} is the density of fluid, kg/m^3.

In International System of units the coefficient of dynamic viscosity η is measured in [Pa·s] ([1 Pa·s] = [1 kg·m^{-1}·s^{-1}] = [1 N·s·m^{-2}]) and the coefficient of kinematic viscosity ν is measured in [m^2·s^{-1}]. But in references viscosity usually is expressed in CGS units: the dynamic viscosity η is measured in Poises [P] = [10^{-1} Pa·s] or Centipoises [cP] = [10^{-3} Pa·s] and the kinematic viscosity ν is measured in Stokes [St] = [10^{-4} m^2·s^{-1}] or Centistokes [cSt] = [10^{-6} m^2·s^{-1}].

The fluid viscosity had a great influence on output of pumps used at the bottom and surface drilling equipment and, as well as, on drill's lowering/hoisting rate in bore-hole. The fluid viscosity determines the travel time of drill string and finally the total time of drilling.

Thus, low viscosity is also one of the essential requirements for the drilling fluid. In references there are following recommendations for the choice of the fluid viscosity:

1) ν less than 5 cSt at –32 °C (*Gundestrup et al.*, 1994a);

2) η less than 5 cP in deep bore-holes and less than 20-25 cP in moderate depth holes (≤1000m) (*Gosink et al.*, 1994);

3) η less than 10 cP (*Fujita et al.*, 1994);

4) maximal values of η in the range of 5–10 cP (*Litvinenko et al.*, 1996).

The coefficient of fluid viscosity, as well as, the fluid density depends on temperature and pressure. The viscosity of fluids usually decreases with temperature and increases with pressure, and the estimation of the real viscosity profile in bore-hole is a difficult task.

The rational values of the average drill's lowering/hoisting rate

The ice core drilling technology includes the pulling up of the drill after each run for core and chips recovery. The time of lowering/hoisting operations takes from 50 to 90 % of the total time of drilling (*Vasiliev and Kudryashov*, 1993). Therefore, the increasing of the drill's lowering/hoisting rate is very important for the commercial penetration rate and to the overall cost of the drilling project.

The criterion of the rational value of drill's lowering/hoisting rate is the minimal total time of drilling up to the depth *H*:

$$T(z)\big|_{z=H} \to min.$$

The influence of the drill's lowering/hoisting rate on the total time of drilling is expressed by equation (4) from *Chapter 3*.

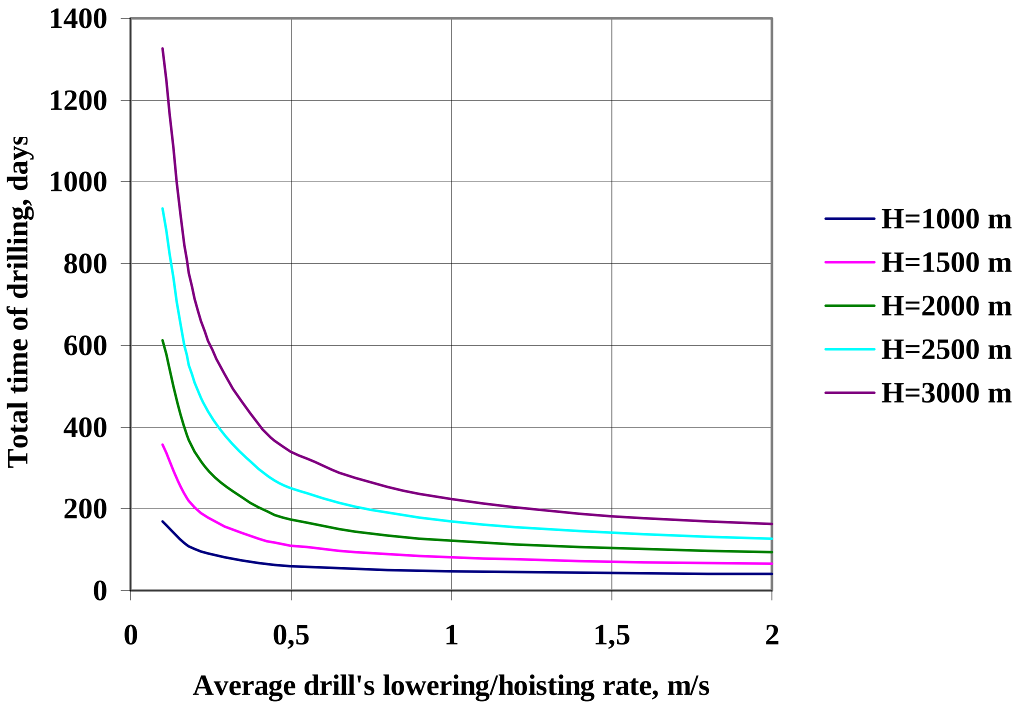
The total time of drilling is calculated (*Fig. 1*) for the following conditions: penetration rate per one run l is 3,4 m; time of drill servicing between runs T_s is 0,35 h; mechanical rate of penetration v_m is 10,1 m/h; coefficient accounting unproductive time k_u is 4,0.

Curves at *Fig. 1* don't have maximums or minimums that can determine the optimal drill's lowering/hoisting rate. Analyze of this curves allows to establish the rational values of this parameter only, when the future increasing of the rate is senseless because it has a very small influence on the total time of drilling. The rational range of the average drill's lowering/hoisting rate depends on the final depth of bore-hole (*Table 1*).

Table 1. The rational range of drill's lowering/hoisting rate.

Final depth of bore-hole, m	**Rational range of average lowering/hoisting rate, m/s**
1000	0,3 - 0,4
1500	0,4 - 0,5
2000	0,5 - 0,6
2500	0,6 - 0,8
3000	0,8 - 1,0

Fig.1. The total time of drilling versus the average rate of lowering/hoisting



According to requirements of the Safety Rules of the Prospecting Drilling (Russia) the maximal lowering/hoisting rate of the drill is 1,0 m/s.

Fluid viscosity and free drill’s lowering rate

The drill is lowered to the bottom of the bore-hole due to the gravity force. This way is very energy economical and simple, but the time of lowering depends on hydrodynamic processes of the drill’s movement in bore-hole.

Onishin et al. (1990) considered the regularities of the free lowering of wire-line drilling tool and recommended the following equation for stabilizing moving (laminar flow between drill and bore-hole walls):

$$v_l = \frac{gD^2}{16\nu}\left[\left(1+k^2\right)\ln k^{-1} - \left(1-k^2\right)\right] \times \left(\frac{4m}{\pi d^2 l \rho_{fl}} - 1\right), \tag{3}$$

where v_l is the free drill's lowering rate in bore-hole, m/s; g is the acceleration gravity, m/s^2; k is the ratio of the drill diameter d and the bore-hole diameter D; ν is the kinematic viscosity of fluid, m^2/s; ρ_{fl} is the density of fluid, kg/m^3; m is the mass of the drill, kg; l is the length of the drill, m. This equation works at $\frac{4m}{\pi d^2 l} > \rho_{fl}$.

In order to determine the relation between the viscosity of the drilling fluid and the free lowering rate, an experiments were carried out at the test side Rikubetsu (Hokkaido) by Japanese scientists (*Fujita et al*., 1994). At the clearance between drill and bore-hole walls 5,5 mm the following empirical equations were obtained:

$$v_l = \frac{1{,}9}{\eta}; \tag{4}$$

$$v_l = \sqrt{\frac{1{,}3}{\eta}}. \tag{5}$$

Equation (4) is a model, when the laminar flow between the drill and the bore-hole walls is dominated. On the other hand, equation (5) is a model, when the turbulent flow between the drill and bore-hole is dominated. Authors intended that the actual relation between the free lowering rate and the viscosity must have components expressed by equations (4) and (5).

Analyze of the equation (3) shows that the free drill's lowering rate depends on parameters of the drill (mass, length, diameter), bore-hole diameter and parameters of the fluid (viscosity and density). The main factors that determined the free drill's rate are the fluid viscosity and the clearance between drill and bore-hole walls.

There are two alternative ways for the achievement of the rational drill's lowering rate. Either a low-viscosity fluid must be used, or bore-holes with larger clearance between drill and bore-hole walls must be drilled.

The free drill's lowering rate is calculated (*Fig. 2; Table 2*) for the following parameters: bore-hole diameter D is 0,13 m; diameter of the drill d is 0,118, 0,116 or 0,114 m (it means that the clearance between drill and bore-hole walls is 6, 7 or 8 mm, respectively); length of the drill l is 11 m; mass of the drill m is 130 kg; density of the fluid ρ_{fl} is 930 kg/m^3. Equation (3) works if the drill's mass m is higher than 104 kg (at d = 0,114 m), 108 kg (at d = 0,116 m) and 112 kg (at d = 0,118 m). For the achievement of the free lowering rate of 1,0 m/s the kinematic viscosity should be less than 0,93 cSt at clearance of 6 mm, less than 1,85 cSt at clearance of 7 mm and less than 3,37 cSt at clearance of 8 mm.

Fig.2. Free drill's lowering rate versus kinematic viscosity of the drilling fluid

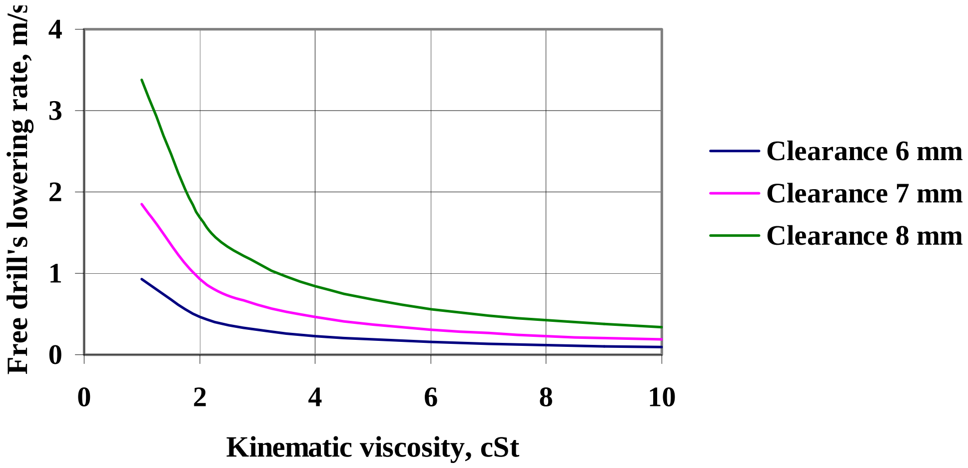


Table 2. Free drill’s lowering rate versus kinematic viscosity of the hole fluid

Lowering rate, m/s	**Kinematic viscosity, cSt**		
	Clearance 6 mm	**Clearance 7 mm**	**Clearance 8 mm**
0,1	9,27	18,54	33,76
0,2	4,63	9,27	16,88
0,3	3,09	6,18	11,25
0,4	2,31	4,63	8,44
0,5	1,85	3,71	6,75
0,6	1,54	3,09	5,62
0,7	1,32	2,65	4,82
0,8	1,15	2,32	4,22
0,9	1,03	2,06	3,75
1,0	0,93	1,85	3,37

The experimental drilling at Hans Tausen Ice Cap, North Greenland, with EPICA drill (*Table 3*) showed that at fluid viscosity of near 3 cSt and average clearance of 7 mm the free lowering rate was 0,6 m/s (*Journe*, 1996). This value is very closure to calculated lowering rate (see *Table 2*). *Zagorodnov et al*. (1994) calculate the rate of lowering for antifreeze thermal electric drill according to (3), and experimental data are in good agreement too. This allows to recommend equation (3) for prognosis of the drill’s lowering rate.

For increasing of the free lowering rate at the upper part of the EPICA drill chip chamber a special valves were installed and hydraulic resistances were reduced. This improving allowed to increase the free lowering rate up to 1,32 m/s.

Table 3. The technological characteristics of ice core drilling by EPICA drill on Hans Tausen Ice Cap (*Journe*, 1996)

Characteristics	Interval, m	
	100 – 218	**218 - 350**
Diameter of drill head, mm outer inner	 132 98	 129,6 98 (or 97,6)
Outer core barrel outer diameter, mm length, m	 118 4,2	
Chips camber outer diameter, mm length, m	 118 and 114 3,8	
Upper part of the drill (electronic section and cable termination) outer diameter, mm length, m	 114 2,8	
Average rate of lowering, m/s with closed valves with opened valves	 0,60 1,32	
Average rate of hoisting, m/s with force 4 kN with force 5 kN	 0,88 1,05	

Viscosity of drilling fluids *versus* temperature

The standard viscosity of fluids is regulated by various national and producing terms (*Table 4*). Viscosity of water at 20 °C under standard atmospheric pressure is 1,002 cP and this value is to be used as the absolute value of the viscosity of water for calibration purposes.

The viscosity temperature coefficient k_t is used in USA mainly as the factor that shows viscosity change with temperature (the smaller coefficient k_t, the lower fluid viscosity changes):

$$k_t = 1 - \frac{\nu_{210}}{\nu_{100}}, \tag{6}$$

where ν_{210} and ν_{100} is the kinematic viscosity at 210 °F (~98,9 °C) and 100 °F (~37,8 °C), respectively.

Table 4. Standard viscosity of drilling fluids (under atmospheric pressure)

Name	Temperature, °C	Dynamic viscosity, cP	Kinematic viscosity, cSt	References
Hydrocarbons				
Fuel DF-A	40	-	1,1-2,4	*Diemand*, 1991
Fuel TS-1	20	-	1,27-1,48	*Dubovkin et al.*, 1985
Fuel Jet A-1	-20	-	4,3	*Diemand*, 1991
Fuel JP-8	-20	-	4,3	*Diemand*, 1991
Exxol D60	25	1,29	-	*Producer's data*
Exxol D40	25	0,96	-	*Producer's data*
Exxol D30	25	0,75	-	*Producer's data*
Densifiers – ethylene hydrocarbons				
Trichlorethylene	20	0,58	-	*Promyshlennye hlororganicheskiye soedineniya*, 1978
Perchlorethylene	20	0,88	-	*Promyshlennye hlororganicheskiye soedineniya*, 1978
Densifiers - chlorofluorocarbons				
CFC 11	20	0,444	-	*Bogdanov et al.*, 1976
CFC 113	25	0,65	-	*Producer's data*
HCFC 123	25	0,45	-	*Producer's data*
HCFC 141b	25	0,416	-	*Producer's data*
HCFC 225ca	25	0,59	-	*Producer's data*
Alcohols, ethers and other organic liquids				
Ethylene glycol	20	19,9	-	*Handbook of Chemistry and Physics*, 1976
Ethanol	20	1,2	-	*Handbook of Chemistry and Physics*, 1976
Octanol	20	10	-	*EPICA Drilling Group*, 1994
n-Butyl acetate	20	0,732	-	*Handbook of Chemistry and Physics*, 1976
Anisole	20	1,32	-	*Handbook of Chemistry and Physics*, 1976
Silicon oils				
KF96-1,5cs	25	-	1,53	*Producer's data*
KF96-2,0cs	25	-	2,07	*Producer's data*

The dynamic viscosity η [cP] and the kinematic viscosity ν [cSt] of the most organic liquids *versus* temperature t_K [K] can be estimated according to (*Dubovkin et al.*, 1985):

$$\lg\lg(\eta+1)=\frac{A}{t_K}-B, \tag{7}$$

and

$$\lg\lg(\nu+1)=\frac{C}{t_K}-D, \tag{8}$$

where *A*, *B*, *C* and *D* are empirical coefficients.

Viscosity–temperature equations (*Table 5*) are based on the experimental data and cover a wide temperature range to enable the determination of fluid viscosity at any desired temperatures in bore-hole. Common units are used for the viscosity (Centipoises for dynamic viscosity η and Centistokes for kinematic viscosity ν).

Table 5. Empirical viscosity-temperature equations

Fluid	Empirical equations	Temperature interval, °C	References
Hydrocarbons			
Fuel DF-A	$\lg\lg(\nu+1)=\frac{403,2}{t_K}-1,74$	-41/19	*N.Gundestrup*, unpublished
Fuel TS-1	$\lg\lg(\nu+1)=\frac{387,2}{t_K}-1,75$	-60/20	*Dubovkin et al.*, 1985
Fuel Jet A-1	$\lg\lg(\nu+1)=\frac{408,6}{t_K}-1,75$	-40/20	*Gundestrup et al.*, 1984
Solvent IP-1200	$\lg\lg(\eta+1)=\frac{384,7}{t_K}-1,73$	-60/-10	*Fujita et al.*, 1994
Exxol D60	$\lg\lg(\nu+1)=\frac{415,3}{t_K}-1,83$	-55/25	*Gundestrup et al.*, 1994a
	$\lg\lg(\nu+1)=\frac{361}{t_K}-1,57$	-47/23	*P.Talalay*, unpublished
Exxol D40	$\lg\lg(\nu+1)=\frac{379,6}{t_K}-1,8$	-55/25	*Gundestrup et al.*, 1994a
Exxol D30	$\lg\lg(\nu+1)=\frac{340,5}{t_K}-1,71$	-55/25	*Gundestrup et al.*, 1994a
	$\lg\lg(\nu+1)=\frac{292}{t_K}-1,46$	-49/23	*P.Talalay*, unpublished
Densifiers			
Trichlorethylene	$\lg\lg(\nu+1)=\frac{260}{t_K}-1,72$	-60/20	*Promyshlennye hlororganicheskiye soedineniya*, 1978
Perchlorethylene	$\lg\lg(\nu+1)=\frac{266,3}{t_K}-1,63$	-20/20	*Promyshlennye hlororganicheskiye soedineniya*, 1978
CFC 11	$\lg\lg(\eta+1)=\frac{312,6}{t_K}-1,87$	-40/0	*Bogdanov et al.*, 1976
HCFC 123	$\lg\nu=\frac{316,1}{t_K}-1,5$	-45/25	*P.Talalay*, unpublished
HCFC 141b	$\lg\lg(\eta+1)=\frac{216,65}{t_K}-1,54$	-80/20	*EPICA Drilling Group*, 1994

HCFC 225ca	$\lg\lg(\eta+1)=\frac{270,5}{t_K}-1,41$	-65/-22	*N.Azuma*, personal communication
Other organic liquids and aqueous solutions			
Ethanol	$\lg(\eta+1)=\frac{589,1}{t_K}-1,75$	-98/0	*Handbook of Chemistry and Physics*, 1976
Aqueous ethanol solution (C_M = 0,5)	$\lg(\eta+1)=\frac{1772,3}{t_K}-5,62$	-40/-20	*Industrial Solvents Handbook*, 1991
Aqueous ethanol solution (C_M = 0,7)	$\lg(\eta+1)=\frac{1388,9}{t_K}-4,43$	-50/-20	*Industrial Solvents Handbook*, 1991
Ethylene glycol	$\lg\lg(\nu+1)=\frac{516,2}{t_K}-1,65$	-10/40	*Industrial Solvents Handbook*, 1991
Aqueous ethylene glycol solution (C_V = 0,5)	$\lg\lg(\nu+1)=\frac{614,3}{t_K}-2,26$	-20/40	*Industrial Solvents Handbook*, 1991
Aqueous ethylene glycol solution (C_V = 0,7)	$\lg\lg(\nu+1)=\frac{545,9}{t_K}-1,91$	-20/40	*Industrial Solvents Handbook*, 1991
n-Butyl acetate	$\lg\lg(\eta+1)=\frac{363,5}{t_K}-1,87$	-47/20	*Gosink et al.*, 1994
Anisole	$\lg\lg(\eta+1)=\frac{287,2}{t_K}-1,41$	0/40	*Handbook of Chemistry and Physics*, 1976
Mixtures			
Fuel Jet A-1 + perchlorethylene (C_V=0,103)	$\lg\lg(\nu+1)=\frac{405,8}{t_K}-1,79$	-45/-5	*Gundestrup et al.*, 1984
Solvent IP-1200 + HCFC 225ca (C_V = 0,2)	$\lg\lg(\eta+1)=\frac{289,6}{t_K}-1,39$	-58/-19	*N.Azuma*, personal communication
Exxol D60 + HCFC 141b (C_M=0,317)	$\lg\lg(\nu+1)=\frac{334,5}{t_K}-1,6$	-44/25	*P.Talalay*, unpublished
Exxol D60 + HCFC 123 (C_M=0,25)	$\lg\lg(\nu+1)=\frac{331,7}{t_K}-1,56$	-45/23	*P.Talalay*, unpublished
Exxol D30 + HCFC 141b (C_M=0,342)	$\lg\lg(\nu+1)=\frac{284,2}{t_K}-1,53$	-48/23	*P.Talalay*, unpublished
Exxol D30 + HCFC 123 (C_M=0,276)	$\lg\lg(\nu+1)=\frac{283,4}{t_K}-1,51$	-47/24	*P.Talalay*, unpublished
n-Butyl acetate + anisole (C_V=0,1)	$\lg\lg(\eta+1)=\frac{324,5}{t_K}-1,68$	-48/25	*Gosink et al.*, 1994
Silicon oils			
KF96-1,5cs	$\lg\nu=\frac{785,6}{t_K}-2,51$	-58/-10	*Fujita et al.*, 1994
KF96-2,0cs	$\lg\nu=\frac{582,2}{t_K}-1,65$	-51/25	*P.Talalay*, unpublished

Yaws C.L. (1994) used another, more complicated equation for dynamic viscosity η [cP] of liquids:

$$\lg \eta = A + \frac{B}{t_K} + Ct_K + Dt_K^2 , \tag{9}$$

where t_K is the temperature, K; *A*, *B*, *C*, and *D* are empirical coefficients (*Table 6*).

Table 6. Empirical coefficients in equation (9) (*Yaws C.L.*, 1994)

Name	**Empirical coefficients**				**Temperature range, K**	
	A	***B***	***C***	***D***	min	max
Densifiers						
Trichlorethylene	-5,5389	7,8313E+02	1,2849E-02	-1,3292E-05	250	571
Perchlorethylene	-7,4654	1,1063E+03	1,6888E-02	-1,5458E-05	251	620
CFC 11	-8,7050	9,7314E+02	2,6505E-02	-3,1615E-05	170	471
CFC 113	-1,8516	4,1245E+02	3,2446E-03	-7,4593E-06	237	487
Other organic liquids						
Ethylene glycol	-16,9728	3,1886E+03	3,2537E-02	-2,4480E-05	261	645
Ethanol	-6,4406	1,1176E+03	1,3721E-02	-1,5465E-05	240	516
n-Butyl acetate	-8,3884	1,3075E+03	1,7671E-02	-1,6145E-05	275	579
Anisole	-8,8307	1,4337E+03	1,7992E-02	-1,5096E-05	287	642

The viscosity of two-compound fluid in a contradistinction to density isn’t in direct proportionality to densifier concentration. The viscosity of oil mixtures is calculated usually according to the following equation:

$$\lg \nu_{mix} = (1 - C_M) \lg \nu_1 + C_M \lg \nu_2 . \tag{10}$$

where ν_{mix}, ν_1 and ν_2 are the kinematic viscosity of mixture, first oil and second oil, respectively; C_M is the mass concentration of second oil.

Preliminary calculations showed that this equation gives a satisfactory agreement (2-10 %) with tests for drilling types of fluid (mixtures of petroleum hydrocarbon liquids with densifiers) at temperatures above –30 °C. But with reducing of temperature the difference between calculated and measured viscosity of mixture achieves 20-30 %.

The prognosis of mixture viscosity due to viscosity of compounds at low temperatures is unreliable. Therefore, it is necessary to test viscosity of two-compound fluid at each concrete concentration of densifier.

According to equations of *Table 5* the kinematic viscosity of drilling fluids is calculated (*Tables 7* and *8*). Dynamic viscosity is converted to kinematic viscosity.

Table 7. Experimental (by italic font) and calculated kinematic viscosity [*cSt*]

Fluid	**Temperature, °C**							
	0	**-10**	**-20**	**-30**	**-40**	**-50**	**-60**	**-70**
Hydrocarbons								
Fuel DF-A	2,55	3,22	***4,26***	5,86	8,67	-	-	-
Fuel TS-1	***1,89***	2,32	***2,95***	3,90	***5,42***	8,08	***13,33***	-
Fuel Jet A-1	2,62	3,33	4,41	6,15	9,21	-	-	-
Solvent IP-1200	3,33	3,89	4,65	5,71	7,23	9,55	13,31	-
Exxol D60	***2,15***	***2,63***	3,37	4,61	***6,70***	10,65	-	-
Exxol D40	***1,47***	***1,79***	2,20	2,83	***3,75***	5,37	8,26	-
Exxol D30	***1,21***	***1,45***	1,70	2,09	***2,73***	3,51	4,92	7,43
Densifiers								
Trichlorethylene	0,48	0,53	0,59	0,66	0,76	0,89	1,06	-
Perchlorethylene	0,66	0,74	0,84	-	-	-	-	-
CFC 11	***0,355***	***0,393***	***0,443***	***0,510***	***0,604***	0,711	0,864	1,081
HCFC 123	0,45	0,50	0,56	0,63	0,72	0,83	-	-
HCFC 141b	***0,402***	***0,434***	***0,471***	***0,516***	***0,571***	***0,639***	***0,723***	***0,832***
Other organic liquids and solutions								
Ethylene glycol	52,4	-	-	-	-	-	-	-
Aqueous ethylene glycol solution (C_V = 0,5)	8,7	14,9	29,5	-	-	-	-	-
Aqueous ethylene glycol solution (C_V = 0,7)	16,1	28,5	-	-	-	-	-	-
Ethanol	1,97	2,58	3,38	4,45	5,90	7,94	10,86	15,18
n-Butyl acetate	***1,21***	1,30	***1,41***	1,78	2,23	2,88	3,93	-
Anisole	***1,77***	2,03	2,41	2,91	-	-	-	-
Mixtures								
Fuel Jet A-1 + perchlorethylene (C_V=0,103)	2,16	2,71	3,52	4,80	6,95	-	-	-
Exxol D60 + HCFC 141b (C_M=0,317)	1,66	1,97	2,39	2,99	3,89	5,30	-	-
Exxol D60 + HCFC 123 (C_M=0,25)	1,85	2,20	2,69	3,38	4,43	6,09	-	-
Exxol D30 + HCFC 141b (C_M=0,342)	1,10	1,26	1,46	1,72	2,07	2,57	-	-
Exxol D30 + HCFC 123 (C_M=0,276)	1,21	1,38	1,60	1,89	2,29	2,86	-	-
n-Butyl acetate + anisole (C_V=0,1)	1,24	1,42	***1,55***	1,99	2,44	3,08	-	-
Silicon oils								
KF96-1,5cs	2,31	2,97	3,90	5,24	7,21	10,20	-	-
KF96-2,0cs	3,03	3,65	4,47	5,56	7,04	9,11	-	-

Table 8. Fixed kinematic viscosity of drilling fluids at negative temperatures [℃]

Name	**Kinematic viscosity, cSt**								
	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Hydrocabons									
Fuel DF-A	-	-7,1	-18,0	-25,3	-30,6	-34,8	-38,1	-40,9	-43,2
Fuel TS-1	-2,8	-20,6	-30,8	-37,7	-42,7	-46,6	-49,7	-52,3	-54,5
Fuel Jet A-1	-	-5,8	-16,7	-24,0	-29,3	-33,4	-36,7	-39,5	-41,8
Solvent IP-1200	-	-9,1	-24,3	-34,1	-41,2	-46,6	-50,9	-54,4	-57,4
Exxol D60	1,5	-15,6	-25,6	-32,3	-37,2	-41,0	-44,1	-46,6	-48,8
Exxol D40	-15,7	-32,2	-41,7	-48,1	-52,8	-56,4	-59,4	-61,8	-63,8
Exxol D30	-27,8	-44,5	-54,0	-60,4	-65,1	-68,7	-71,6	-74,0	-76,0
Other organic liquids									
Ethanol	-0,5	-15,6	-26,1	-34,1	-40,5	-45,8	-50,2	-54,1	-57,4
n-Butyl acetate	-35,2	-51,3	-60,5	-	-	-	-	-	-
Mixtures									
Fuel Jet A-1 + Perchloretylene (C_V=0,103)	2,4	-14,0	-24,3	-31,2	-36,3	-40,2	-43,3	-46,0	-
Exxol D60 + HCFC 141b (C_M=0,317)	-10,8	-30,1	-41,0	-48,3	-	-	-	-	-
Exxol D60 + HCFC 123 (C_M=0,25)	-4,6	-24,9	-36,4	-44,0	-49,6	-	-	-	-
Exxol D30 + HCFC 141b (C_M=0,342)	-38,3	-56,4	-	-	-	-	-	-	-
Exxol D30 + HCFC 123 (C_M=0,276)	-33,0	-52,0	-	-	-	-	-	-	-
n-Butyl acetate + Anisole (C_V=0,1)	-30,2	-48,9	-59,5	-	-	-	-	-	-
Silicon oils									
KF96-1,5cs	6,1	-10,3	-20,9	-28,5	-34,4	-39,1	-43,1	-46,5	-49,5
KF96-2,0cs	-	0,6	-14,6	-25,3	-33,3	-39,8	-45,0	-49,5	-

The viscosity of densifiers - chlorofluorocarbons and ethylene hydrocarbons - at negative temperatures is very low (less than 1 – 1,5 cSt). In mixture with petroleum liquids densifiers decrease the total viscosity significantly. This consideration was confirmed by experiments carried out in Copenhagen University (*Fig. 3* and *4*).

One of the main causes that kept back the use of aqueous solutions of ethylene glycol and ethanol is their very high viscosity (see *Tables 7* and *9*). Therefore, *Zagorodnov et al.* (1994) suggest to drill bore-holes filled by aqueous ethanol solution with larger clearance (10-12 mm) between drill and bore-hole walls. In this case an appropriate free lowering rate (0,5-0,7 m/s) can be achieved even at temperature of –60 °C. The main disadvantages of such larger diameter drilling are more expenditure time of mechanical penetration and more energy consumption.

The same problems were noted in deep ice drilling with aqueous ethylene glycol solution (*Hansen*, 1976). It is impossible to use aqueous ethylene glycol solution at low temperature (less than –30 °C) because the fluid is too viscous.

Fig.3. Viscosity of potential drilling fluids for Central Greenland

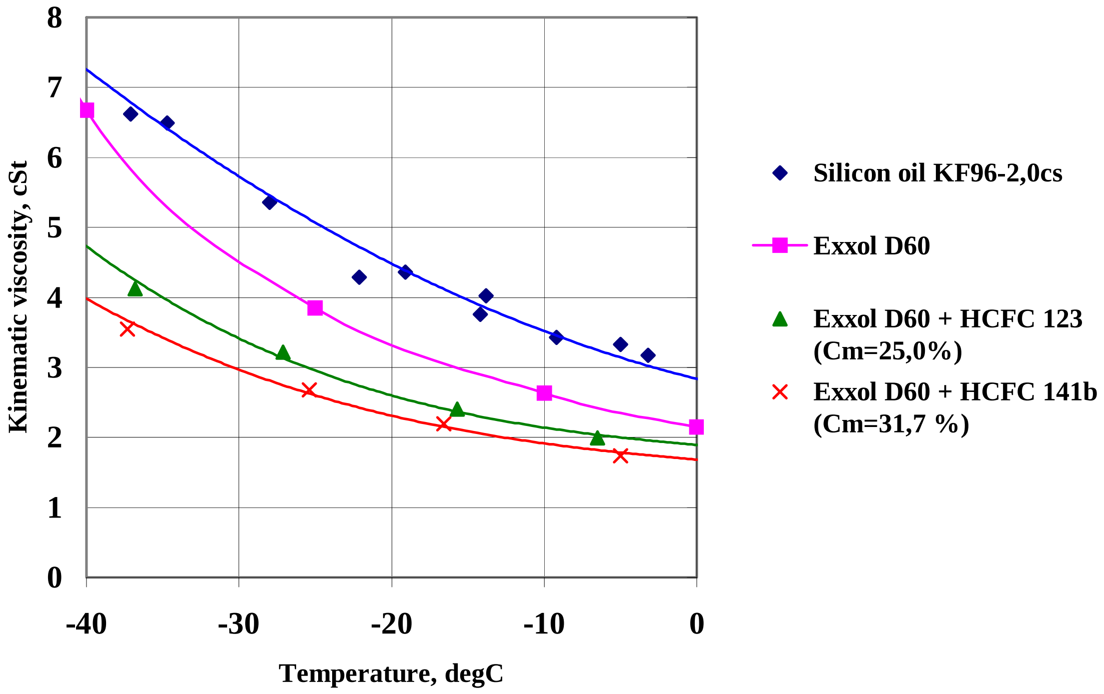


Fig.4. Viscosity of potential drilling fluids for Central Antarctica

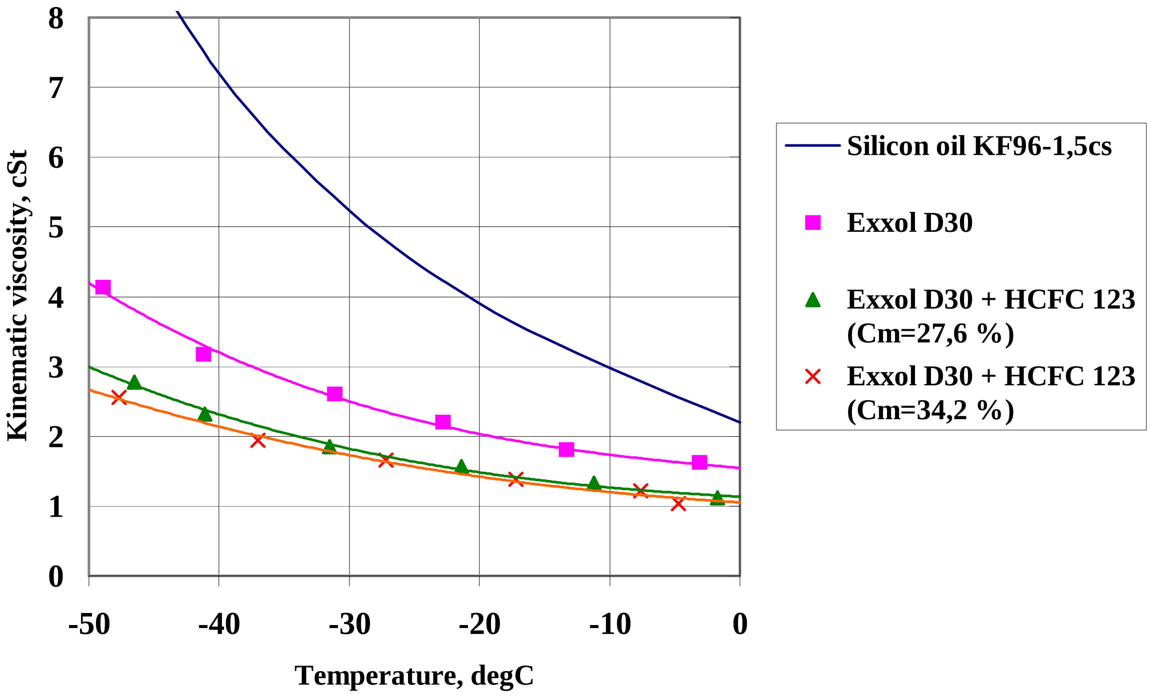


Table 9. Dynamic viscosity [*cP*] *of ethanol* (*Hanbook of Chemistry and Physics,* 1976) *and aqueous ethanol solutions* (*Industrial Solvents Handbook,* 1991)

Fluid	**Temperature, °C**					
	0	**-10**	**-20**	**-30**	**-40**	**-50**
Ethanol (C_M = 0,99)	1,7	2,1	2,8	3,7	5,0	6,8
Aqueous ethanol solution (C_M = 0,7)	3,5	6,0	10,4	18,1	32,6	-
Aqueous ethanol solution (C_M = 0,5)	6,4	12,1	23,2	46,0	-	-

Silicon oils of KF96 series have lowest variation in viscosity with temperature among all types of silicon oils, mineral oils and synthetic fluids. The viscosity of silicon oils KF96-1,5cs and 2,0cs is less than viscosity of aqueous solutions of ethylene glycol and ethanol but it is rather high too (viscosity of KF96-1,5 cs is about 10 cSt at –50 °C, and viscosity of KF96-2,0cs is about 5,6 cSt at –30 °C).

Viscosity of drilling fluids *versus* pressure

The estimation of the exact viscosity of drilling fluid under the high pressure in the bore-hole is very difficult because of the limited experimental data devoted to this problem. Some experiments were made by *Fujita et al.* (1994). It was observed that a steel ball installed to the special sell with drilling fluid (n-butyl acetate and solvent IP-1200) was shaken under a pressures up to 50 MPa and temperatures up to –60 °C. But actual values of fluid viscosity weren't measured.

Dubovkin et al. (1985) recommend following equation for viscosity of petroleum oil liquids under pressure:

$$\lg\frac{\eta}{\eta_0} = 1{,}42\times10^{-7}(P-P_0)(0{,}0239+1{,}117\times10^{-4}\eta_0) \qquad (11)$$

where η and η_0 are the viscosity under pressure P [Pa] and standard atmospheric pressure P_0 (P_0 = 101 325 Pa), respectively, cP.

According to equation (11) the viscosity of Exxol type D solvents increases on 26,4 % under the pressure of 30 MPa (*Fig. 5*). An approximate viscosity profile of mixture of solvent D60 with densifier HCFC 123 (C_M = 0,25) is shown at *Fig.6* at assumptions that viscosity of mixture submitted to equations (10) and (11). The temperature profile is taken for the conditions of Central Greenland (GRIP) and hydrostatic pressure is calculated according to equation (18) of *Chapter 2*.

Fig.5. Viscosity of Exxol solvents under pressure at temperature 15 degC

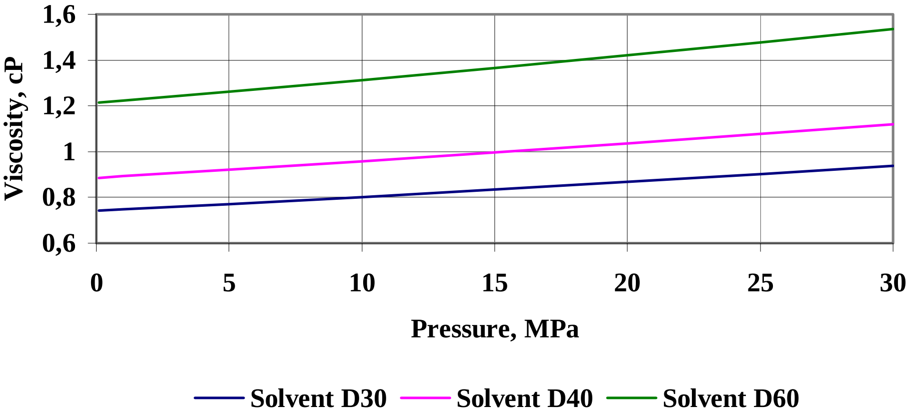
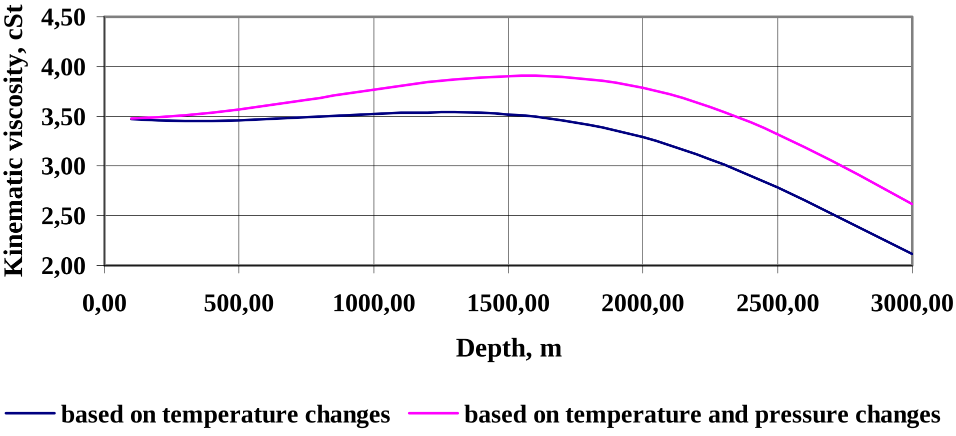


Fig.6. Viscosity profile in 3000-m bore-hole in Central Greenland (drilling fluid: mixture D60 with densifier HCFC 123, Cm=25,%)



Due to the calculated viscosity we can intend the free drill’s lowering rate for EPICA drill with closed valves to be 0,5-0,6 m/s in the upper part of the bore-hole and 0,7-0,9 m/s at the depths below 2000 m.

Resume

Estimation of the real viscosity profile in bore-hole is impracticable now. Before additional information about the viscosity of two-compound fluids and influence of pressure on viscosity is obtained, the choice of the fluid viscosity should includes the following steps:

1. At first, the rational range of average drill's lowering/hoisting rate is estimated according to equation (4) from *Chapter 3*.
2. The maximal value of fluid viscosity is calculated according to equation (3) for the concrete parameters of the drill and for given free lowering rate.
3. According to intended bore-hole temperature and to the maximal value of fluid viscosity the drilling fluid can be chosen (*Tables 4-9*).
4. If viscosity of the chosen fluid is higher than maximal value, the technology of drilling should be improved for reducing of hydraulic resistance during drill's movement in bore-hole (for example, additional flowing through the drill, enlarging of the hole, etc.).

The mixtures of fuel TS-1 and Exxol solvents with densifiers, as well as, n-butyl acetate have the most suitable viscosity for deep ice drilling.

5. FROST-RESISTANCE

Frost-resistance is one of the main technological characteristics of drilling fluid used at negative temperatures. Drilling fluid cannot be used below its freezing point. Therefore, the freezing point of fluid should be higher not only the minimal temperature in bore-hole but the temperature of air outside drilling shelter too (where the fluid is usually stored). This is important especially for drilling sites in Central Antarctica (for example, the average annual temperature at Vostok Station is –57 °C and the absolute temperature minimum is –89,2 °C).

The cloud point is the temperature at which wax crystals begin to precipitate out of hydrocarbon fuel. The cloud point is specified for diesel fuels only.

The pour point is the temperature at which the fluid doesn't flow during 5 seconds from the glass inclined on 45°. The pour point is specified for liquid hydrocarbons, fuels and oils. If the fluid is stirred continually, its pour point is decreased on 10-30 °C than pour point at static condition (*Dubovkin et al.*, 1985).

The freezing point (melting point) is the temperature, at which the solid and liquid phases of a substance can exist in equilibrium together at a defined pressure (normally at standard atmospheric pressure of 101 325 Pa, *Table 1*). The freezing point slightly increases with pressure growth (for example, the freezing point of ethanol increases from –114,1 °C at standard atmospheric pressure to –108 °C at pressure of 100 MPa).

Eutectic point is the temperature at which the mixture of two or more liquids solidifies as a whole, when cooled, without change in composition. Eutectic point is the lowest freezing point of the mixture.

The freezing point given for jet fuels and other hydrocarbon liquids is the temperature at which first crystals are formed in a chilled fluid and seen with the naked eye. In order to increase the fuels production from crude oil, the specified frost-resistance requirements are reduced. For example, at the beginning of 1950th according to ASTM D1655 the specified freezing point of turbine fuel Jet A-1 was –55 °C and now it is –47 °C only.

The freezing point t_{fr} of two-compound fluid is between freezing points of components. For example:

(a) freezing point of mixture of Jet A1 (t_{fr} = -47 °C) with 10,3 % perchlorethylene (t_{fr} = -22,3 °C) is below –40 °C (*Gundestrup et al.*, 1984);

(b) freezing point of mixture of n-butyl acetate (t_{fr} = -78 °C) with 10 % of anisole (t_{fr} = -37,4 °C) is below –49 °C (*Gosink et al.*, 1989).

Table 1. Frost-resistance of drilling fluids at standard atmospheric pressure

Name	Pour point, °C	Freezing point, °C	References
Hydrocarbons			
Fuel DF-A	-57	-51*	*Diemand*, 1991
Fuel Jet A1	-51	-47	*Diemand*, 1991;
Fuel JP-8	-54	-46	*Diemand*, 1991;
Fuel TS-1	-	-60	*Dubovkin et al.*, 1985
Exxol D60	-	-57	*Talalay*, unpublished
Exxol D40	-	<-55	*Gundestrup et al.*, 1994a
Exxol D30	-	<-55	*Gundestrup et al.*, 1994a
Densifiers – halogenated hydrocarbons			
Trichlorethylene	-	-86,4	*Industrial Solvents Handbook*, 1991
Perchlorethylene	-	-22,3	*Industrial Solvents Handbook*, 1991
Densifiers - fluorocarbons			
CFC 11	-	-111	*Handbook of Chemistry and Physics*, 1976
CFC 113	-	-35	*Handbook of Chemistry and Physics*, 1976
HCFC 123	-	-107	*Producer's data*
HCFC 141b	-	-103,5	*Producer's data*
HCFC 225ca	-	-131	*Producer's data*
Other organic liquids			
Ethylene glycol	-	-12,6	*Industrial Solvents Handbook*, 1991
Ethanol	-	-114,1	*Industrial Solvents Handbook*, 1991
n-Butyl acetate	-	-78	*Gosink et al.*, 1989
Anisole	-	-37,4	*Gosink et al.*, 1989
Silicon oils			
KF96-1,5cs	-76	-	*Producer's data*
KF96-2,0cs	-84	-	*Producer's data*

*The cloud point

It is well known that for decreasing of the cloud point of diesel fuels they are blending with kerosene usually (*Diemand*, 1991):

$$I_{bl} = (1 - C_V) I_{df} + C_V I_k \ , \tag{1}$$

where I_{bl}, I_{df} and I_k is the cloud point index of the blend, diesel fuel and kerosene, respectively; C_V is the concentration of kerosene in the blend.

The cloud point index I is connected with cloud point t_{cl} [°C] by the following equation:

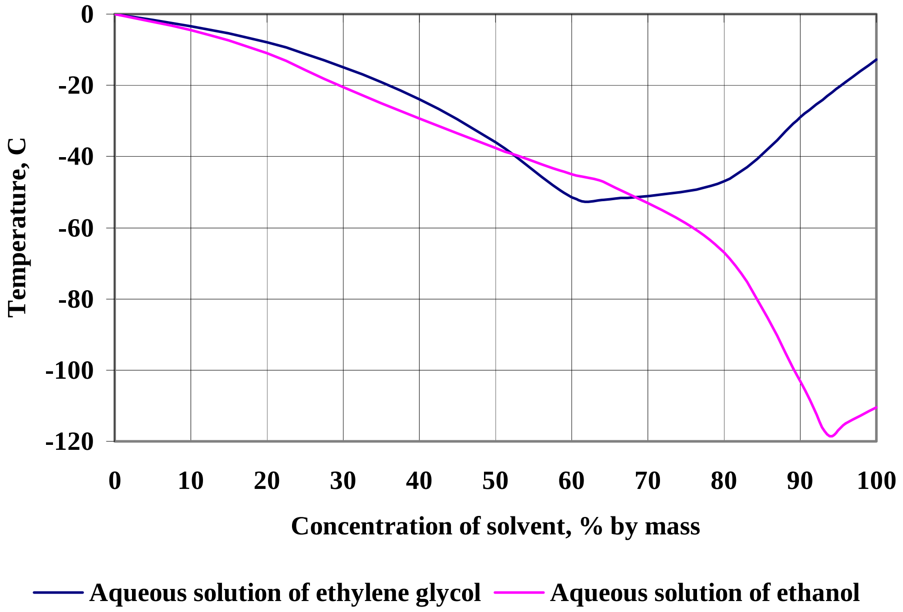
$$\lg I = 0{,}0327 t_{cl} + 2{,}264 \, . \tag{2}$$

The freezing point of aqueous solutions of ethylene glycol and ethanol depends on the concentration of the solvent (*Table 2, Fig. 1*). At first, the freezing point of aqueous solutions of ethylene glycol and ethanol decreases with concentration of solvent and then has a minimum at C_M = 0,65 (t_{fr} ≅ -52 °C) and C_M = 0,935 (t_{fr} ≅ -118 °C), respectively. These temperatures are eutectic points for aqueous solutions of ethylene glycol and ethanol. Then the freezing point increases.

Table 2. Freezing point [℃] *of aqueous solutions* (*Handbook of Chemistry and Physics*, 1976 *and Industrial Solvents Handbook*, 1991)

Mass concentration, %	**Aqueous solutions of ethylene glycol**	**Aqueous solutions of ethanol**
10	-3,37	-4,47
20	-7,93	-10,92
30	-15	-20,47
40	-23,84	-29,26
50	-36	-37,67
60	-51,53	-44,93
68	-45,3	-49,52
80	-47	-67
90	-29	-103
96	-19	-115

Fig. 1. Freezing points of alcohol aqueous solutions



6. STABILITY

Stability of drilling fluids during storage and transportation

Stability is the property of drilling fluid not to change properties during storage, transportation and use in bore-hole.

Some types of hydrocarbons containing by petroleum products are able to react with air oxygen and metals and form resinous or solid sediments. This process is more active during abrupt temperature changing. In general, stability of petroleum products depends on their composition. The turbine fuels that are produced by the direct distillation from crude oil are more stable than products containing cracking-compounds.

In the tanks with volume 25 – 30 m^3 the resin content in turbine fuel TS-1 achieves the standard maximal level after 5 years of storage, in tanks of smaller volume the products of oxidizing are formed more quickly (*Dubovkin et al.*, 1985).

Stability of homogeneous liquids is very high under specified conditions. Most of the liquids, especially densifiers – fluorocarbons, used for ice drilling have a high rate of vaporization (see Chapter "*Volatility*"). Moreover, the fluid storage in opened or not fully tanks causes the dissolving of water containing in air and the changing of the fluid properties (see chapter "*Solubility*"). Therefore, storage tanks should be kept full and hermetically sealed when not in use.

Stability of drilling fluids in bore-hole

Stability of drilling fluids in bore-hole it isn't sufficiently tested.

Most of the drilling fluids for ice core drilling consist from two or more components (petroleum product + densifier or solvent + water). Mutual solubility of the compounds of drilling fluid depends on the chemical nature of the compounds (see Chapter "*Solubility*"). In general, liquids are miscible because of their chemical similarity and, *vice verse,* liquids are immiscible because of their chemical difference.

Stability of two-compound mixture of petroleum product with densifier – fluorocarbon can be estimated on the example of mixture of fuel TS-1 with densifier CFC 11 according to density measurements *in situ* that were carried out in the deep bore-hole 3G at Vostok station.

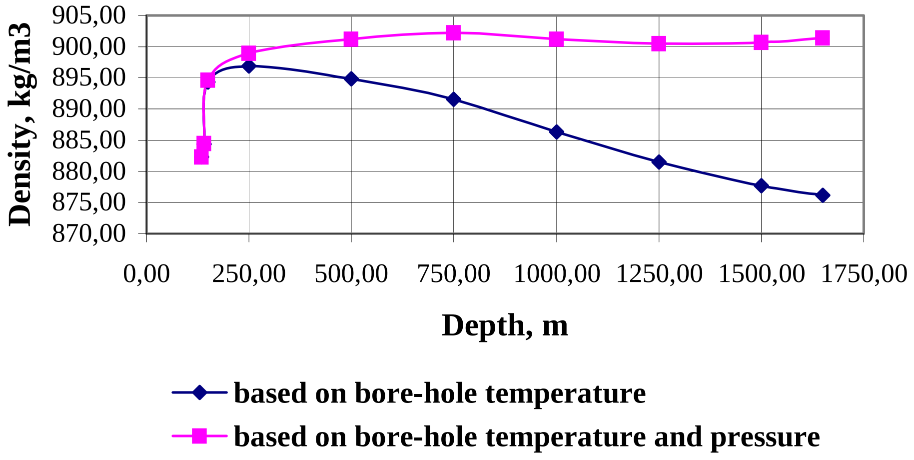
In 1986, the drilling of the bore-hole 3G was stopped at the depth of 2202 m when the thermal drill was stuck in the interval 1935 – 1943 m during the hole enlarging. After 8 years, in January of 1994, the fluid samples were taken from different depths of 3G bore-hole by a special probe; and on the surface the density of the hole fluid was measured at certain temperature. The volume and mass concentrations of the densifier were calculated (*Table 1*) according to equations (23) and (24) of *Chapter 2*.

Table 1. Concentration of densifier in 3G bore-hole, Vostok Station (January, 1994; V.K.Chistyakov, personal communication)

Depth, m	**Bore-hole temperature, °C**	**C_V, %**	**C_M, %**
140	-56,2	4,1	7,5
150	-56,1	5,3	9,7
250	-55,4	5,7	10,4
500	-53,5	5,6	10,3
750	-51,4	5,4	9,9
1000	-49,0	5,0	9,2
1250	-46,3	4,7	8,6
1500	-43,4	4,5	8,3
1650	-41,4	4,4	8,2

Then the density of bore-hole fluid is estimated for two different cases: density based on temperature and density based on temperature and compressibility (*Fig. 1*). The method of calculations is expounded in *Chapter 2*.

Fig.1. Density porofile in 3G bore-hole (Vostok Station) according to density of samples



The analyzing of data at *Table 1* and curves on *Fig.1* allows to conclude the following:

1) the density of the drilling fluid in consequence of the densifier concentration is almost the same (~900 kg/m^3) at the most part of the hole, that probably is the evidence of the density vertical equalization during long standing (during drilling the quantity of adding densifier wasn't stable);
2) after long standing of two-compound mixture of fuel TS-1 with CFC 11 the densifier isn't precipitated to the bottom of the bore-hole;
3) at the upper 100 m part of the fluid column density of the fluid is rather smaller than in lower part of the hole, that probably was caused by vaporization of densifier from the top of the fluid (densifiers – fluorocarbons have extremely high rate of vaporization).

Unfortunately, we don't have the density profile in 3G bore-hole directly after the drilling in order to compare with density after standing during 8 years. Anyway, this mixture is rather stable in bore-hole that allows to carry out the bore-hole geophysical measurements until present.

The first and the second foregoing conclusions doesn't confirm by the temperature measurements at GRIP bore-hole (1994) made with very high resolution. This measurements shows that the natural convection of the fluid in bore-hole exists only at the limited interval of about 20 m. Therefore, the movement of the fluid over this interval should occur very slowly that preserve compounds from rising or lowering.

Hydrophilic liquids in bore-hole isn't stable because they are characterized by spontaneous dissolving of ice bore-hole walls. This cause decreasing of the solvent concentration and the formation of the slush in bore-hole. We don't have a data confirming the long stability of aqueous ethylene glycol or ethanol solutions; on the contrary, bore-hole at Byrd station filled by aqueous ethylene glycol solution (*Ueda and Garfield*, 1969) and bore-hole at Novolazarevskaya Station filled by aqueous ethanol solution (*Kudryashov et al.*, 1991) were plugged by slush soon after the drilling.

7. COMPATIBILITY WITH POLYMERS AND METALS

Compatibility of drilling fluids with elastomers and plastics

Drilling fluid should be non-aggressive to the drill and cable components. One of the main problems is to choose material for gaskets and electrical insulation (lacquer on wire, plastic jacket of wire, insulation of electrical sockets, etc.) that isn't swell, soften or become tacky in fluid. The reference data regarding to compatibility of different solvents with elastomers or plastics indicates often the abbreviation or trademark of polymer.

Abbreviations for the names of elastomers and plastics have been proposed by many national and international organizations (American National Standards Institute, *ANSI*; American Society for Testing Materials, *ASTM*; British Standards, *BS*; International Organization for Standardization, *ISO*; etc.). Some abbreviations were introduced by law, others are trademarks in certain countries. As a result the same compound is characterized by different abbreviations. The following *Table 1* includes the most widespread abbreviations and trademarks for elastomers and plastics.

Table 1. Abbreviations for elastomers and plastics (Polymer Handbook, 1989)

Abbreviation or trademark	Name	Abbreviation or trademark	Name
Elastomers		***Plastics***	
ABS	Acrylonitrile-butadiene-styrene rubber	**Bakelite®**	Phenolic resins
ACM	Acrylate (polyacrilate) rubber	**CA**	Cellulose acetate
AU	Urethane rubber (polyester)	**CN,** **Nitron®**	Cellulose nitrate (nitrocellulose)
BR	Butadiene rubber	**Nylon 6,** **Capron® 8220**	Polyiminocarbonyl pentamethylene (Polyamide 6)
Buna® N	Acrylonitrile butadiene rubber	**Nylon 66,** **Zytel® 101**	Haxamethylendiamine adipate
Buna® S	Butadiene styrene rubber	**PBT**	Polybutylene terephthalate
CR	Chloroprene (polychloroprene) rubber	**PC,** **Lexan®**	Polycarbonate
CSM	Chlorosulphonated polyethylene	**PCTFE**	Polychlorotrifluoroethylene
ECO, **CO**	Epichlorohydrin rubber	**PE**	Polyethylene
EPDM **EPM, EPR**	Ethylene propylene rubber	**PEHD**	Polyethylene with high density
EU	Urethane rubber (polyether)	**PELD**	Polyethylene with low density

FPM, **Silastic®**	Fluororubber	**PET,** **Lavsan®**	Polyethylene terephthalate
GN	Neoprene rubber	**PMMA,** **Plexiglas®**	Polymethyl methacrylate (Acrylate, Organic glass)
Hycar®, **Latex®**	Polydimethyl siloxane	**POM**	Polyoxymethylene
IIR	Isoprene isobutene (butyl) rubber	**PP**	Polypropylene
IR	Isoprene rubber	**PPO**	Polyphenylene oxide
MFQ	Fluorosilicone rubber	**PS**	Polystyrene
NBR	Nitrile (nitrile butadiene) rubber	**PTFE** **Teflon®, Halon® TFE**	Polytetrafluoroethylene
NR, **Thiokol® NVT**	Natural rubber	**PVA**	Polyvinyl alcohol
PU	Polyurethane	**PVC**	Polyvinyl chloride
Q,	Polydimethyl siloxane rubber (Silicone rubber)	**PVDC**	Polyvinylidene chloride
SBR	Styrene rubber	**PVDF,** **Kynar® 18**	Polyvinylidene fluoride
T, **Thiokol®**	Polysulphide rubber	**Victrex®**	Polyethersulphone
		Viton®	Benzene nexachloride

Effect of potential drilling fluids on elastomers and plastics specified in *Table 2* refers to the room temperature. The table doesn't indicate what effect the fluid may have on the chemical stated. Therefore, it is necessary to give following comments to the proposed classification.

Recommended materials are unlikely to be destroyed in the fluid.

Materials with minor to moderate effect will probably give satisfactory results but will sooner or later be destroyed by the fluid.

Materials with moderate to serve effect may be used to a certain extern in conjunction with the indicated fluid if the contact period is short. Permanent contact will, however, destroy the material.

Not recommended materials will be destroyed soon after the contact with the fluid.

Aromatics containing in ***petroleum products*** tend to cause swelling and degradation of certain rubber materials. That is one of the reasons to limit maximum acceptable concentration of aromatics in turbine fuels on 20 – 25 %. The concentration of aromatics in solvents of Exxol type is not more than 0,5 %; therefore, effect of this type of petroleum products on elastomers is less than in common fuels.

Table 2. Compatibility of drilling fluids with elastomers and plastics (Gosink et al., 1991; *Industrial Solvents Handbook,* 1991; *Diemand,* 1991; SKEGA Co., *Eramark, Sweden*; *Producer's data)*

Name	**Recommended materials**	**Minor to moderate effect**	**Moderate to serve effect**	**Not recommended materials**
		Petroleum products		
Diesel fuel	NBR, ECO, T, MFQ, FPM, ACM, Teflon, Viton	CR, CSM, AU	PP	NR, IR, SBR, BR, IIR, EPDM, Q
Kerosene	NBR, ECO, MFQ, FPM, ACM	AU, T	CR, CSM	NR, IR, SBR, BR, IIR, EPDM, Q
Fuel JP-8	Nitriles (Krynac, Hycar, Chemigum), Fluorosilicones (Silastic), Fluorocarbons (Kel-F, Fluorel, Vition, Teflon), Nylon			
Exxol D30, D40, D60	PE, PP, polyester materials, Teflon			NR, BR, EPDM, PS
		Densifiers		
Trichlorethylene	FPM	AU, MFQ		NR, IR, SBR, BR, IIR, EPDM, NBR, T, ACM
Perchlorethylene	T, FPM, PP, Teflon, Viton	ECO, Q, MFQ	NBR	NR, IR, SBR, BR, IIR, EPDM, CR, CSM, AU,
CFC 11	NBR, CSM, T, FPM, PVA, PVDC, Nylon, Bakelite, PTFE, PMMA	CR, MFQ, CA, CN, PVC	PE	NR, IR, SBR, BR, IIR, EPDM, AU, Q
CFC 113	NBR, ECO, CR, CSM, T, PU, ABS, PC, PTFE, PP, PVC, PMMA, Nylon, Victrex, Bakelite, PVDF, PS, PVA, PVDC	SBR, BR, AU, FPM, CA, CN, PE	NR, IR, PPO	IIR, EPDM, Q, MFQ, PS
HCFC 141b	ABS, IIR, ACM, CR, Viton, Bakelite, Nylon, PBT, PET, PTFE, PVC, Rislan	PP, PEHD, NBR, Pebax 6533	EPDM, PC, Viton A,	NR, ABS, Q, GN, PMMA, PS Pebax 2533
HCFC 225	PVC, PC, POM, ABS, Nylon 6, Nylon 66, PET, PTFE, PCTFE, ECO, Bakelite	PELD, PEHD, PP		PMMA
		Other liquids		
Ethylene glycol	NR, IR, SBR, BR, IIR, EPDM, NBR, ECO, CR, CSM, Q, MFQ, FPM	AU	T	ACM
Ethanol	NR, IR, SBR, BR, IIR, EPDM, ECO, CR, CSM, T, Q, MFQ, FPM	NBR, AU		ACM

n-Butyl Acetate	PP, Teflon, PE, Kevlar, Nylon	IIR, EPDM, Viton	T	ECO, CR, CSM, Q, MFQ, FPM, ACM, “Cumar” resins, dammar, ester gum, mastic, rosin, synthetic resins (vinyl polymers, PS, acrylates)
Anisole	NR, PP, Teflon, Viton			
Silicon oils	NR, IR, SBR, BR, IIR, EPDM, NBR, ECO, CR, CSM, AU, T, MFQ, FPM, ACM		Q	

There is a wide range of materials for seals and O-rings, which can operate in various petroleum fuels and other liquids of kerosene type (*Table 2*). O-ring and seals composed of nitriles, fluorocarbons and fluorosilicones are commercially available for most of applications and are commonly designed for use down to at least –40 °C. Nitrile rubber (NBR) is probably the most common compound used in seals because of its good resistance to petroleum oils and its wide temperature range.

Silicon rubber (Q) remains flexible down to very low temperatures but is not suitable for use with petroleum fuels. Nylon and Teflon are compatible with petroleum oils, and they are commonly used as backup rings to give skeletal strength to some seals. This becomes increasingly important in low-temperature applications many of the compounds used for the primary seal are relatively soft and are prone to excessive abrasion and similar damage.

Gundestrup et al. (1994) and *P.Talalay* (unpublished) tested compatibility of petroleum solvent Exxol D80, densifiers CFC 113, HCFC 123, HCFC 141b, n-butyl acetate and silicon oil KF96-2,0cs with two elastomers: ethylene propylene rubber (EPDM) and nitrile rubber (NBR). The O-ring gaskets were exposed to fluids during 24 hours at 25 °C (*Table 3*). Silicon oil KF96-2,0cs is the only fluid that doesn’t react with these elastomers.

Table 3. Changes [%] *in O-ring gaskets after immersion in drilling fluids during 24 hrs* (*Gundestrup et al.*, 1994; *P.Talalay*, unpublished)

Fluid	EPDM	NBR
Exxol D80	34	1
CFC 113	17	3
HCFC 123	16	33
HCFC 141b	14	20
n-Butyl acetate	10	26
Silicon oil KF96-2,0cs*	0	0

*No visible changes during a week

Densifiers – ***trichlorethylene and perchlorethylene*** are very aggressive solvents and they have various effects on the most elastomers and plastics (*Table 2*). Fluororubber (FPM) is the only elastomer that can operate in these liquids.

Table 4. Changes [%] *in elastomer samples after immersion in densifiers CFC 11 and CFC 113* (*Industrial Solvents Handbook*, 1991)

Elastomer	**CFC 11**			**CFC 113**		
	Length	**Weight**	**Extraction**	**Length**	**Weight**	**Extraction**
Neoprene rubber	-4,5	-8,2	Weight loss and coloration of solvent	-4,9	-5,7	Weight loss and coloration of solvent
Navy gum rubber	-4,6	-10,0	Weight loss and coloration of solvent	-4,3	-9,5	Weight loss and coloration of solvent
Buna N rubber	-5,2	-10,9	Weight loss and coloration of solvent	-4,0	-10,5	Weight loss
Ebonite rubber	-1,8	-3,5	Fairly low	-1,7	-3,3	Fairly low weight loss
Pure gum rubber	-2,7	-3,8	Fairly low	-1,4	-3,8	Fairly low weight loss

Table 5. Changes [%] *in plastic samples after immersion in densifiers CFC 11 and CFC 113* (*Industrial Solvents Handbook*, 1991)

Plastic	**CFC 11**					**CFC 113**				
	Width	**Length**	**Thickness**	**Weight**	**Effect of solvent**	**Width**	**Length**	**Thickness**	**Weight**	**Effect of solvent**
Bakelite	0,0	0,0	0,0	0,0	None	-0,3	-0,2	0,0	0,0	Virtually none
CA	0,0	0,4	0,0	4,9	Fin. wt 98,5 % of original	0,0	0,0	0,8	1,6	Final wt. 99,7 % of original
CN	0,5	0,6	0,8	5,2	Fin. wt 98 % of original	-0,4	0,0	0,0	1,7	Final wt. 99,5 % of original
PTFE	0,0	0,0	1,5	1,4	Fin. wt 100,5 % of original	-0,6	0,0	1,5	1,2	Final wt. 100,5 % of original
PVDF	-	-	-	-	-	0,0	0,0	0,0	0,0	None
PC	-	-	-	-	-	0,0	0,0	0,0	0,0	None
Nylon 6	0,0	0,0	0,0	0,0	None	0,0	0,0	0,0	0,0	None
PMMA	0,0	0,0	0,0	0,0	None	0,0	-0,2	0,0	0,0	Virtually none
PE	6,1	6,7	7,6	32,4	Fin wt. 101 % of original	2,6	2,3	3,4	12,1	Fin. wt. 101 % of original
PS	-	-	-	-	Sample disintegrated	0,0	-0,2	0,0	0,0	Virtually none
PVA	0,7	0,3	0,8	0,4	Virtually none	0,0	-0,1	0,8	0,0	Virtually none
PVC	0,2	0,0	0,7	11,5	Fin. wt 110 % of original	0,6	0,0	0,8	0,0	Virtually none
PVDC	0,1	0,1	0,8	0,0	Virtually none	-0,1	0,1	0,8	0,0	Virtually none
Nylon 66	0,0	0,0	0,0	0,0	Virtually none	-0,1	0,0	-0,8	0,0	Virtually none

Densifiers – ***fluorocarbons*** cause swelling or dissolving of the most types of elastomers and plastics (*Tables 2 – 6*). Problems can be experienced with natural rubber (NB), ethylene propylene rubber (EPDM), silicon rubber (Q), polystyrene (PS), polymethyl methacrylate (PMMA) and other polymers.

Table 6. Compatibility of HCFC 141b and HCFC 365mfc with some plastics and elastomers (*weight change* [%] *after one week immersion at 25 °C*)

Material	**HCFC 141b**	**HCFC 365mfc**
Plastics		
PVC	0,77	-0,02
PEHD	7,1	0,37
PMMA	Dissolved	57
PC	23	0,27
PP	12,5	0,16
Nylon 66	1,87	-0,33
PBT	0,17	0,15
PS	Dissolved	0,19
Elastomers		
GN	87	1,02
Viton A	46	90,5
EPDM	44	1,62
NR	185	7,14
NBR	47	2,46
Q	110	16,1

Drilling fluids – alcohols (***ethylene glycol*** and ***ethanol***) have no effect on the most elastomers (*Table 2*).

n-Butyl acetate is very aggressive solvent. There are no elastomers that can able operate in n-butyl acetate during long time (*Table 2*). Even, butyl rubber (IIR) and ethylene propylene rubber (EPDM) are slightly destroyed in n-butyl acetate; and IIR cannot be used at low temperatures (*Gundestrup et al*., 1994).

Gosink et al. (1991) considered that n-butyl acetate has no effect on the various materials employed in the PICO deep drill string. However, during drilling at Summit (GISP2 Project) it was necessary to abandon the cable after three seasons in field because of n-butyl acetate affecting to the tensile strength of the Kevlar cable used in PICO's drilling operations.

Silicone oils are compatible with the most plastics and elastomers (*Table 2*). But the low-molecular silicone oils with viscosity less than 10 cS can extract the plasticizers contained in some types of rubber and plastic, and cause weight and volume loss or smelling. Experiments carried out in Copenhagen University showed that there no visible changes in O-rings gaskets (EPDM and NBR) after immersion in silicon oil KF96-2,0cs during a week (see *Table 3*).

Compatibility of drilling fluids with metals

Petroleum products don't react with carbide and stainless steel, but non-ferrous metals aren't recommended for use in the hydrocarbon fuels (*Table 7*).

Table 7. Acceptable and unacceptable metals for use with hydrocarbon fuels (*Diemand*, 1991)

Satisfactory	Unsatisfactory
Aluminum and all its alloys	Bronze
Carbon molybdenum steel	Nickel
0,5-3 % nickel steel	Copper
4-6 % chromium molybdenum steel	Zinc
300 and 500 series stainless steel	Cadmium
Monel	Brass

At ordinary temperatures ***perchlorethylene*** can be used with common construction metals; it becomes aggressive to metals at temperatures over 140 °C.

CFC 113 is compatible with the most metals and alloys (*Tables 8, 9*). Problems can be experienced with zinc: the zinc samples were slightly tarnished after exposure in CFC 113 during week.

Table 8. Decomposition of CFC 113 solvent exposure to metal samples (*Industrial Solvents Handbook*, 1991)

Metal	Time, days	Decomposition, %
Mild steel	360	0,95
Stainless steel 316	430	0,25
Incotel	435	0,21
Nickel	300	0,31
Monel	250	1,03
Copper	300	0,032
Zinc	300	0,043
Tin	300	0,039

HCFC 123 isn't aggressive to steel (that is a specified material for packing). The following materials should be avoided: alkaline metals and their alloys, strong alkaline desiccatives, ferric chloride, some molecular sieves, alkaline-earth metals, metallic powders. Contact with strong bases or alkaline materials may provoke violent reactions or explosions.

Table 9. Compatibility of CFC 113 and HCFC 225 with metals
“Corrosion Appearance” (7 days at boiling point)

Metal	CFC 113	HCFC 225
Aluminum	None	None
Magnesium	None	None
Zinc	Slight tarnish	None
Cooper	None	None
Stainless steel	None	None
Steel	None	None
Tin	None	None

HCFC 141b has no effect on the most metals and alloys commonly used in industry (steel, iron, stainless steel, copper, bronze). However, light metals (zinc, beryllium, aluminum, magnesium) may be attacked during long-term exposure with HCFC 141b in the presence of water.

HCFC 225 don’t corrode metals and alloys (*Table 9*). Incompatible materials are strong oxidizers and alkaline earth metals.

8. VOLATILITY

The problem of volatility isn’t simple. On the one hand, the high volatility of drilling fluid raises the human health and fire safety questions. For liquids with the high rate of vaporization it is necessary to organize careful control of air contamination and ensure the threshold limits in air (see Chapter “*Toxicological and environmental requirements*”) and minimal inflammable concentration (see Chapter “*Flammability*”). From this point of view the using of fluid with low rate of vaporization is preferably.

On the other hand, there are benefits of the high volatility. The work place and clothes became clear after a short time, and the ice core is easy to handle.

Rate of vaporization (the process of change into a vapour or into a gaseous state) per unit surface area of liquid at temperature t_K is given by (*Penguin Dictionary of Physics*, 1991):

$$\frac{dm}{dt} = \alpha P \sqrt{\frac{M}{2\pi R t_K}} , \qquad (1)$$

where P is the vapour pressure of the vapour of relative molecular mass M; R is the universal gas constant (R= 8,314 J/(K·mol)); α is the vaporization coefficient that is less than unity.

Usually rate of vaporization of liquids is estimated in relative units in comparison with vaporization of diethyl ether, n-butyl acetate, acetone and other chemicals.

Saturated vapour pressure (or “***vapour pressure***”) at given temperature is the pressure exerted by a vapour in equilibrium with its liquid. The vapour pressure of liquids reflects its volatility. The variation of vapour pressure p with temperature t_K over limited temperature ranges is given by Kirchhoff formula (*Penguin Dictionary of Physics*, 1991):

$$\log p = a - \frac{b}{t_K} - c \log t_K , \qquad (2)$$

where a, b and c are empirical constants.

In references the units of vapour pressure are [kPa], [mm Hg] = [0,1333 kPa], [bar] = [100 kPa], [kg/cm^2] = [98, 066 kPa]. In *Table 1* the references data are transformed to [kPa].

Boiling point is the temperature of a liquid at which visible evaporation occurs through the bulk of the liquid, and which the vapour pressure of the liquid equals the external atmospheric pressure. It is the temperature at which liquid and vapour can exist together in equilibrium at a given pressure. The boiling point is commonly restricted at standard atmospheric pressure (101 325 Pa).

Table 1. Volatility properties of drilling fluids (Handbook on Chemistry and Physics, 1994; Sax's dangerous properties of industrial materials, 1996; producer's data)

Fluid	Vapour pressure at temperature, kPa	Specific density of vapours (air = 1)	Boiling point, °C	Relative rate of vaporization
Oil hydrocarbons				
Diesel fuel DF-A	0,6 / 38 °C	-	-	-
Kerosene	-	4,5	175 – 325	-
Fuel Jet A1	1,4 / 38 °C	-	205 - 290	-
Fuel JP-8	1,4 / 38 °C	-	205 - 290	-
Exxol D60	0,1 / 20 °C 0,2 / 38 °C 0,4 / 50 °C	>1	190 – 221	4 (n-BuAc = 100)
Exxol D40	-	>1	145 – 200	14 (n-BuAc = 100)
Exxol D30	-	>1	130 - 166	44 (n-BuAc = 100)
Densifiers				
Trichlorethylene	0,6 /-20 °C 1,2 / -9 °C 2,3 / 0 °C 7,5 / 20 °C	4,53	86,7	40 (ether = 100)
Perchlorethylene	0,6 / 0 °C 1,9 / 20 °C 2,5 / 25 °C	5,83	121,2	9 (ether = 100) 280 (n-BuAc =100)
CFC 11	88,2 / 20 °C 107 / 25 °C	4,7	23,7	160 (acetone = 100)
CFC 113	37,8 / 20 °C 44 / 25 °C	6,2	47,7	123 (ether = 100)
HCFC 123	76,3 / 20 °C 91,4 / 25 °C	5,3	27,1	-
HCFC 141b	64 / 20 °C 81 / 25 °C	-	32,1	-
HCFC 225	21,6 / -10 °C 26,7 / 0 °C 33,5 / 10 °C 43,0 / 20 °C	-	54	90 (ether =100)
Other liquids				
Ethylene glycol	0,008 / 20 °C 0,016 / 25 °C	2,14	197,5	-
Ethanol	5,9 / 20 °C 7,9 / 25 °C	1,59	78,3	-
n-Butyl acetate	1,2 / 20 °C 2,0 / 25 °C	4,0	126,5	-
Anisole	0,4 / 25 °C 1,3 / 42 °C	-	153,8	-
Silicone oil KF96-1,5cs	-	-	194	-
Silicone oil KF96-2,0cs	-	-	229	-

If it is known the boiling point t_b [°C] at non-standard pressure P [mm Hg], the correctness of boiling point Δt_b [°C] to standard pressure may be obtained from the following equation (*Handbook of tables for organic compound identification*, 1967):

$$\Delta t_b = \frac{(273{,}1 + t_b)(2{,}8808 - \log P)}{S + 0{,}15(2{,}8808 - \log P)}, \tag{3}$$

where S is the entropy of vaporization at standard pressure (it may be estimated from the graph and the table in reference).

Oil products consist from compounds with a wide range of boiling points. Therefore, the boiling point given for fuels has a wide range too (see *Table 1*). Petroleum producers often specify "***distillation volume***" that is the temperature at which the certain part (10 %, 50 %, or 90 %) of the oil products will boil off (*Table 2*). ***End point*** (or "***dry point***") is the temperature at which no liquid remains.

Table 2. Distillation volume of low-temperature fuels and solvents of Exxol type (*Deimand*, 1991; *Producer's data*)

Fuel or solvent	**Distillation volume, °C**			**End point, °C**
	10 %	**50 %**	**90 %**	
DF-A	-	-	288	330,3
Jet A1	190,2	212	250	266,3
JP-8	190,2	212	250	266,3
Exxol D60	-	-	209	215
Exxol D40	-	169	-	188
Exxol D30	-	150	-	164

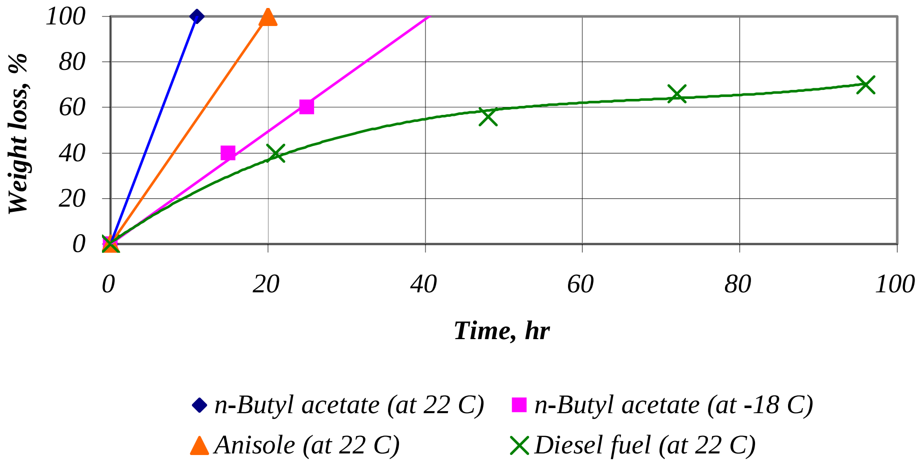
The lighter, more volatile compounds will boil off at the lower temperatures of the 10 – 50 % levels, while the heavier ones will not boil until a much higher temperature. Thus, a lower temperature at any of the levels implies a lighter, more volatile oil products, while the spread between the 10 % level and the end point reflects incidentally the relative amount that can be obtained from the parent crude oil.

The vaporization rate of oil products isn't linear (for example, diesel fuel at *Fig. 1* or solvent Exxol D60 at *Fig. 3*). The lighter compounds are evaporated faster than heavier ones.

Solvents of Exxol D type have more homogeneous composition and the difference of distillation volumes (20 – 40 °C) is rather narrow than fuels (80 – 150 °C).

The boiling point of kerosene type liquids used for ice core drilling is about 200 °C and the rate of vaporization is low (for example, the vaporization rate of solvent Exxol D60 is in 25 times lower than the rate of n-butyl acetate). The content of the most harmful aromatic hydrocarbons in Solvents of Exxol type is less then 0,5 %. This means that the vapours isn't so hazard and nearly without odor.

Fig. 1. Evaporation of potential drilling fluids (5 ml of solvent in a 50-ml beaker, Gosink et al., 1989)



The vaporization of densifiers - halogenated hydrocarbons (trichlorethylene, perchlorethylene) are rather high and their vapours are very hazard to human health (threshold limits are 25 – 50 ppm only). These liquids can be used with strong precautions and sufficient ventilation of working area.

Densifiers - fluorocarbons have the lowest boiling points and the highest rate of vaporization. These type of liquids is nonflammable and threshold limits of air contamination are high (500 – 1000 ppm). The main problem connected with fluorocarbon's volatility is the harm for the ozone layer.

Ethylene glycol has the very high boiling point and the very low vapour pressure. It means that it is evaporated very slowly. Boiling points of aqueous ethylene glycol solutions increase with the growth of solvent concentration (*Table 3*).

The volatility of ethanol is good in terms of a land spill and cleanness of ice core, but leads to concern with respect to fire hazard. The boiling points of aqueous ethanol solutions are in the range of 78 – 100 °C (see *Table 3*).

The rate of vaporization of n-butyl acetate at –18 °C is higher than the rate of vaporization of diesel fuel at 22 °C (*Fig. 1*). The advantages of this are that any unexpected releases or spills should evaporate quickly. The main problem of the volatility of n-butyl acetate is fire and health hazard. *Gosink et al.* (1994) consider that at –20 °C, an average-to-cool day on the drill site, the maximum possible air concentration of n-butyl acetate in unventilated area would be approximately 0,13 %. This concentration is in 8,6 times higher than threshold limit of air contamination (0,015 %).

Table 3. Boiling points of solvents aqueous solutions (*Industrial solvents handbook, 1991*)

Aqueous ethylene glycol solutions		**Aqueous ethanol solutions**	
C_M	**Boiling point, °C**	C_M	**Boiling point, °C**
0	100	0	100
0,1	101	0,05	95,1
0,2	102	0,12	90,5
0,3	103	0,22	86,5
0,4	105	0,39	83,3
0,5	107	0,52	81,7
0,6	110	0,63	80,8
0,7	115	0,79	79,4
0,8	123	0,88	78,7
0,9	137	0,95*	78,1
1,0	197	1,0	78,3

*Azeotropic mixture (the vapour produced by the partial avaporation of liquid has the same composition of liquid)

Silicon oils of KF96 series exhibit very low vapour pressure (below than 0,1 kPa at 20 °C). This means that the use of silicon oils will leads to “greasy” work place and clothes.

In order to compare the vaporization rate of potential drilling fluids, they were tested in University of Copenhagen. Ten samples of liquids (10 ml) were poured out into cylindrical glass with inner diameter 56 mm (area of free surface is equal to 24,6 cm^2) at room temperature (22,5 °C). The mass-loss of the samples was periodically measured with accuracy 0,1 g. For comparison one of the tested liquid was a water.

Densifiers – fluorocarbons (HCFC 123 and HCFC 141b) evaporate very fast (*Fig. 2*). The vaporization rate of HCFC 123 is approximately in 1,5 time higher than the rate of HCFC 141b (*Table 4*).

Two tested mixtures of Exxol D60 with densifiers HCFC 123 and HCFC 141b have the same density (920 kg/m^3 at 22 °C). At the beginning mixtures evaporate very fast but in both cases the vaporization rate is lower than the rate of pure densifiers. Mixture of Exxol D60/HCFC 141b evaporates faster than mixture of Exxol/HCFC 123 because mass concentration of densifier in first mixture (C_M = 0,45) is higher than at second one (C_M = 0,35). The fast vaporization is going up to the moment when densifiers completely evaporate from mixtures and then the vaporization rate is equal to rate pure Exxol D60.

Fig.2. Vaporization rate of potential drilling fluids

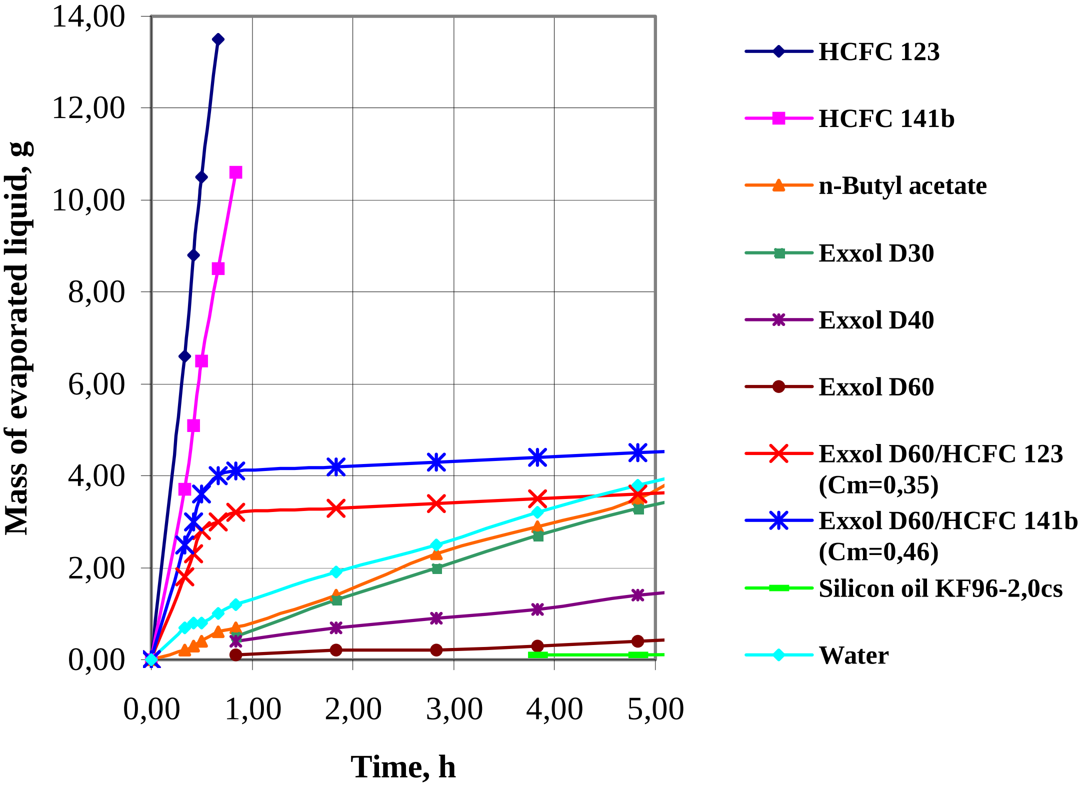
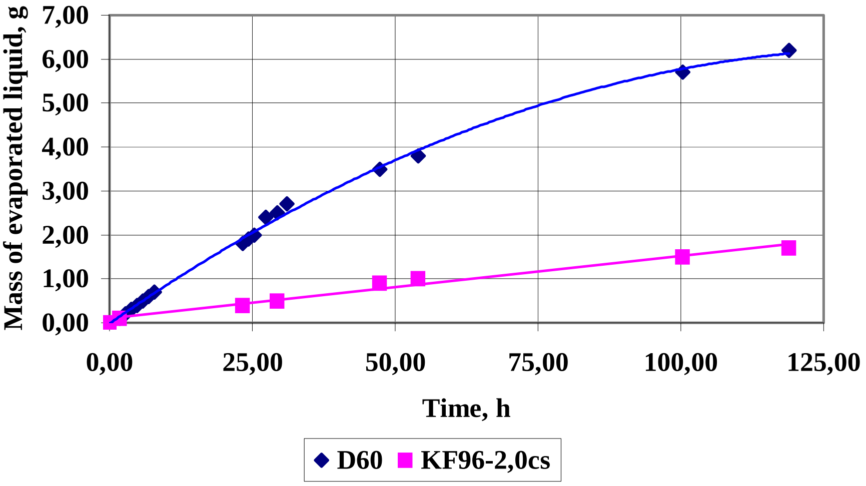


Fig.3. Vaporization rate of solvent Exxol D60 and silicon oil KF96-2,0cs



The vaporization rates of n-butyl acetate and water are very similar.

At first, when the lighter compounds are evaporated from solvent Exxol D30, it has same vaporization rate as n-butyl acetate, but remained heavier compounds evaporated more slowly. Exxol D60 and silicon oil KF96-2,0cs have the lowest rate of vaporization (*Fig. 3*).

The processing of the experimental data gives the gradient of vaporization rate V_g [g/h] and vaporization rate V [g/(h·m^2)]:

$$V_g = \frac{dm}{dT}; \tag{4}$$

$$V = \frac{V_g}{S}, \tag{5}$$

where dm is the mass of evaporated liquid during time dt [h], g; S is the free surface area of liquid, m^2.

In *Table 4* tested liquids are listed in decreasing order of vaporization rate.

Table 4. Vaporization rate of potential drilling fluids at temperature 22,5 °C

Fluid	**V_g, g/h**	**V, g/(h·m^2)**	**Interval of mass-loss, %**	
			from	**to**
HCFC 123	20,66	8133	0	93
HCFC 141b	12,96	5268	0	87
Exxol D60 + HCFC 141b (C_M = 45 %)	7,22	2934	0	35
Exxol D60 + HCFC 123 (C_M = 35 %)	5,57	2264	0	30
n-Butyl acetate	0,736	300	0	40
Water	0,731	297	0	38
Exxol D30	0,700	284	0	45
Exxol D30	0,272	110	48	60
Exxol D40	0,270	110	0	30
Exxol D40	0,146	59,4	60	76
Exxol D60 + HCFC 141b (C_M = 45 %)	0,0926	37,6	44	52
Exxol D60 + HCFC 123 (C_M = 35 %)	0,0926	37,6	35	42
Exxol D60	0,084	34,1	0	36
Silicon oil KF96-2,0cs	0,0142	5,77	0	20

9. FLAMMABILITY

Flash point is lowest temperature at which a substance will provide sufficient inflammable vapour (under special conditions) to ignite upon the application of a small flame.

Closed-cup (the container is closed to the air) and open-cup (the container is opened to the air) techniques are used to obtain flash point. In both methods a given volume of liquid is heated in a prescribed container at a definite rate, and periodically a test flame or spark is passed across the surface of the liquid. The temperature, at which a flame passes across the surface of the liquid, is taken as flash point. Lower values are obtained by means of the closed-cup method than by the open-cup method. Values of boiling point listed in *Table 1* were obtained by the closed-cup method.

The most drilling fluids are dangerous with respect to fire hazard. The flash point of petroleum oil fluids (fuels, solvents of Exxol type) depends on their chemical composition. The turbine fuel TS-1 and solvent Exxol D30 contain more low-molecular-weight hydrocarbons and, therefore, have the low flash point (28 °C).

The flash points of ethanol, ethanol-water solutions and n-butyl acetate is lower than flash points of petroleum drilling fluids.

Limits of flammability (% by vol.) are the extremes in concentration between which vapour – air mixtures can be burned when subjected to an ignition source of adequate temperature and energy.

The flammable range of vapours in air of ethanol is 3,28 – 18,95 % and of n-butyl acetate is 1,39 – 7,55 % (*Handbook of Chemistry and Physics*, 1976).

Gosink et al. (1994) write about the fire safety of n-butyl acetate: ”The lower flame limit concentration of n-butyl acetate in air is 1,4 %. This corresponds to a vapor pressure of 12,9 mm Hg, achievable only in unventilated closed room or container at 24 °C. The warmest part of the drill site days, according to temperature records from past sites, rises to about 0 °C.” Therefore, authors conclude: “The fire hazard of butyl acetate is very low at temperatures below about 0 to 10 °C and, thus, does not pose any inordinate danger.”

Zagorodnov et al. (1994) consider that the same arguments are still marginally true for cold aqueous ethanol. Moreover, the lower flame limit of ethanol (3,28 %) is rather high than limit of n-butyl acetate (1,39 %).

Anyway, ethanol and n-butyl acetate should be used safely as a drilling fluid with respect to fire hazard.

Table 1. Flammable properties of drilling fluids (Diemand, 1991; Gosink et al., 1994; Sax's dangerous properties of industrial materials, 1996; producer's data)

Fluid	**Flash point, °C**	**Auto-ignition temper-ature, °C**	**Label**	**Tools for fighting the fire**
Oil hydrocarbons				
Fuel DF-A	38	225	Flammable Liquid	CO_2, dry chemical
Kerosene	65-85	540	Flammable Liquid	Foam, CO_2, dry chemical
Fuel Jet A1	38	-	Flammable Liquid	Foam, CO_2, dry chemical
Fuel JP-8	46,4	-	Flammable Liquid	Foam, CO_2, dry chemical
Fuel TS-1	28	-	Flammable Liquid	Foam, CO_2, dry chemical
Exxol D60	62	>200	Flammable Liquid	Foam, powder, water
Exxol D40	40	>200	Flammable Liquid	Foam, powder, water
Exxol D30	28	>200	Flammable Liquid	Foam, powder, water
Densifiers				
Trichlorethylene	Nonflammable	420	-	-
Perchlorethylene	Nonflammable	-	-	-
CFC 11	Nonflammable	-	-	-
CFC 113	Nonflammable	-	-	-
HCFC 123	Nonflammable	>650	-	-
HCFC 141b	Nonflammable	532	-	-
HCFC 225	Nonflammable	-	-	-
Other liquids				
Ethylene glycol	111	400	-	Alcohol foam, water, foam, CO_2, dry chemical
Aqueous ethylene glycol solution (C_M = 0,9)	132	-	-	-
Ethanol	12	363	Flammable Liquid	Alcohol foam, CO_2, dry chemical
Aqueous ethanol solution (C_M = 0,5)	22	-	-	-
Aqueous ethanol solution (C_M = 0,3)	28	-	-	-
n-Butyl acetate	22	425	Flammable Liquid	Alcohol foam, CO_2, dry chemical
Anisole	52	475	Flammable Liquid	Foam, CO_2, dry chemical
Silicon oil KF96-1,5cs	min 50	~450	-	-
Silicon oil KF96-2,0cs	min 75	~450	-	-

10. SOLUBILITY

Solubility parameters

Solubility is the property of substance to form with other mixtures, which are chemically and physically homogeneous throughout. In reference to liquid the term "solubility" is often used synonymously with "miscibility".

The degree of solubility (often spoken as "*solubility*") is the concentration of a solute in a saturated solution at given temperature. Solubility of the most substance increases with rise in temperature, but there are cases where a substance is more soluble in cold than in hot solvents.

The solubility of organic compounds can be estimated according to ***Hildebrand solubility parameter*** [MPa^{½}] (*Barton*, 1991):

$$\delta = \sqrt{\frac{\rho_{fl}(\Delta H - Rt_K)}{M}}, \tag{1}$$

where ρ_{fl} is the density of liquid, g/cm^3; ΔH is the enthalpy of vaporization, J/mol; R is the universal gas constant (R = 8,314 J/(mol·K)); t_K is the temperature, K; M is the molecular weight (*Table 1*).

Table 1. Solubility parameters of some drilling liquids at 25 °C (*Barton*, 1991)

Fluid	***M***	***ρ*, g/cm³**	**Δ*H*, kJ/mol**	***δ*, MPa½**
Petroleum oil products				
Kerosene	128 – 198	0,75 – 0,78	-	-
Solvent Exxol D60	145	-	-	-
Solvent Exxol D40	143	-	-	-
Solvent Exxol D30	133	-	-	-
Densifiers				
Trichlorethylene	131,39	1,455	34,54	19,0
Perchlorethylene	165,83	1,611	39,68	20,3
CFC 11	137,37	1,467	24,79	15,4
CFC 113	187,38	1,565	28,08	14,7
HCFC 123	152,93	-	-	-
HCFC 141b	116,95	1,236	-	-
Other liquids				
Ethylene glycol	62,07	1,112	-	32,9
Ethanol	46,07	0,785	42,32	26,5
n-Butyl acetate	116,16	0,876	43,86	17,7
Anisole	108,15	0,989	46,90	19,5
Silicon oil KF96-1,5cs	310,70	-	-	-
Silicon oil KF96-2,0cs	384,86	-	-	-
Water	18,02	0,997	43,98	47,9

A material with a high δ value requires more energy for dispersal than is gained mixing it with a material of low cohesion parameter, so immiscibility results (with the exception of solvents, such as ethanol (δ = 26,5 MPa^{½}) and water (δ = 47,9 MPa^{½}) that are completely miscible when a large difference in δ values exists). On the other hand, two materials with similar δ values gain sufficient energy on mutual dispersion to permit mixing.

For the marking of solubility is often used the following scale: insoluble (less than 1 %), slightly soluble (1 – 5 %), and soluble or miscible (*Table 2*).

Table 2. Solubility of drilling fluids with common solvents (*Hanbook of Chemistry and Physics*, 1976; *Sax's dangerous properties of industrial material*, 1996; *producer's data*)

Name	Insoluble	Slightly soluble	Miscible
Oil hydrocarbons			
Kerosene	Water	-	Pet. solvs
Densifiers			
Trichlorethylene	Water	-	Alcohols, ether, acetone, chloroform
Perchlorethylene	-	Water	Alcohols, ether, benzene and most org. solvs
CFC 113	Water, ethylene glycol	-	Ethanol, ethyl acetate, anisole, acetone
HCFC 123	Water	Most org. solvs	-
Other liquids			
Ethylene glycol	Ether	Benzene	Water, alcohols, acetone, acetic acid, chloroform
Ethanol	-	-	Water, alcohols, ether, chloroform, benzene, acetic acid and most org. solvs
n-Butyl acetate	-	Water	Alcohols, ether, acetone, propylene glycol and most org. solvs
Anisole	Water	-	Alcohols, ether, acetone, benzene
Silicon oils of KF96 type	Water, ethanol, glycol,, glycerin	-	Gasoline, ethers, esters, chloroform

Water solubility

In respect to water all liquids can be divided to

a) ***hydrophobic liquids*** in which water wets a liquid/air boundary surface to some extent and after mixing the water and the liquid form the emulsion (mixture of two or more immiscible liquids);

b) ***slightly soluble liquids***, which are able to dissolve the limited quantity of water;

c) ***hydrophilic liquids*** that can be mixed with water at any concentration and after mixing form the true solution (uniformly dispersed mixture at the molecular or ionic level).

Table 3. Water solubility of drilling fluids under atmospheric pressure

Name	Solubility of water in fluid, % by mass	Solubility of fluid in water, % by mass	References
Petroleum oil products			
Fuel TS-1	0,00865/at 20 °C	-	*Dubovkin et al.*, 1985
Exxol D60	-	<0,1/at 20 °C	*Producer data*
Exxol D40	-	<0,1/at 20 °C	*Producer data*
Exxol D30	-	<0,1/at 20 °C	*Producer data*
Densifiers			
Trichlorethylene	0,02/at 25 °C	0,1/at 25 °C	*Industrial Solvents Handbook*, 1991
Perchlorethylene	1,05/at 25 °C	1,5/at 25 °C	*Industrial Solvents Handbook*, 1991
CFC 11	0,011/at 25 °C	0,011/at 25 °C	*Handbook on Chemistry and Physics*, 1976
CFC 113	0,011/at 25 °C	0,017/at 25 °C	*Handbook on Chemistry and Physics*, 1976
HCFC 123	-	0,39/at 25 °C	*Producer data*
HCFC 141b	-	0,4/ at 20 °C	*Producer data*
Other liquids			
Ethylene glycol	Miscible		*Industrial Solvents Handbook*, 1991
Ethanol	Miscible		*Industrial Solvents Handbook*, 1991
n-Butyl acetate	2,88/ at 25 °C	0,78/ at 25 °C	*Industrial Solvents Handbook*, 1991
Anisole	Insoluble		*Handbook on Chemistry and Physics*, 1976
Silicon oils of KF96 type	Insoluble		*Prospectus* of Shin-Etsu Chemical Co.

Hydrophobic liquids (oil hydrocarbons, fluorocarbons – *Table 3*) are insoluble in water (maximal concentration is less then 1 %). The water content depends not only on chemical composition of the liquid, but on the atmospheric conditions too (temperature, pressure, humidity). With temperature reduction water concentration decreases significantly (*Table 4*). For example, the water concentration in fuel TS-1 decreases in 7,4 times at temperature change from 40 to –10 °C.

Table 4. Water solubility in different fluids versus temperature at standard atmospheric pressure (101325 Pa) and relative humidity equal to 1,0 (*Solubilities of inorganic and organic compounds*, 1963; *Dubovkin et al.*, 1985; *Industrial Solvents Handbook*, 1990)

Trichlorethylene		**Fuel TS-1**		**CFC 113**	
Temperature, °C	**Water solubility, %**	**Temperature, °C**	**Water solubility, %**	**Temperature, °C**	**Water solubility, %**
-38	0,0008	-10	0,00250	0	0,0036
-32	0,0017	-5	0,00315	25	0,0110
-26	0,0030	0	0,00384	30	0,0130
-20	0,0045	5	0,00473		
-14	0,0060	10	0,00580		
-8	0,0078	20	0,00865		
-2	0,0103	30	0,01273		
4	0,0130	40	0,01848		
10	0,0166				
16	0,0214				
22	0,0270				

The water solubility in fuels at ordinary atmospheric pressure and humidity may be estimated according to the following empirical equation:

$$\lg C_t = a \lg t_K + b , \tag{2}$$

where C_t is the water solubility at temperature t_K (K), % by mass; a and b are empirical coefficients (for fuel TS-1 a=11,46 and b=-30,33).

Dubovkin et al. (1985) for the calculation of water solubility in fuels at different atmospheric conditions recommend the following equation:

$$C_{P,t} = C_0 \varepsilon \frac{P}{P_0} \left(\frac{t_k}{t_k^0} \right)^n , \tag{3}$$

where $C_{P,t}$ is the water solubility at atmospheric pressure P (Pa), temperature t_K (K) and relative humidity ε (parts of unity); C_0 is the water solubility at atmospheric pressure P_0=101325 Pa, temperature t_K^0=293 K and relative humidity ε_0=1,0; n is an empirical power (for fuel TS-1 n=11,5).

After mixing of hydrophobic liquids with water the emulsion of “water in oil” or “oil in water” types is formed. Tests carrying out with the mixture of fuel TS-1 with CFC 11 blended with water showed that this emulsion is very unstable, and the water phase is isolated after 24 hours completely (*Pashkevich and Chistyakov*, 1989).

Usually the hole temperatures are lower than the surface temperatures, and, therefore, during the bore-hole filling the water soluble in the liquid on the surface comes out of the solution at first in the tiny condition and then in the form of ice crystals. This effect was noticed at Vostok station where after the each bore-hole filling of approximately 1 m^3 of drilling fluid (mixture of TS-1 with CFC 11 with density 860-880 kg/m^3) “dirty” ice chips were collected at the bottom on the height 0,1 - 0,2 m.

To minimize the effect of water solubility a small quantity of ethanol is added in fuels that are used for engines at low temperatures. The proportion of ethanol is not more than 0,1 % by vol., because larger amount lowers the flash point of fuel and creates the fire hazard (*Deimand*, 1991). This way isn’t suitable for fuels that used as drilling fluids because ethanol dissolves not only water suspended in fluid but it will dissolve ice from bore-hole walls too.

The maximal water solubility in ***slightly soluble liquids*** (for example, perchlorethylene, n-butyl acetate) is 1 – 5 %.

For the decreasing of the ice crystals condensed from the bore-hole fluid the following considerations should be taken into account:

1. The more liquid is in the tank, the smaller will be the volume of air from which moister can be condensed. Therefore, tanks should be kept full when not in use.
2. The use of heating fluid or the fluid that is taken from the warm areas isn’t recommended.
3. Some amount of water or ice crystals may be collected on the bottom of the fuel tanks or at the surface of the densifier in the storage drums. The simplest method is not to use the lower or the upper layers of the fluid containing ice crystals. On the other hand different kind of filters refining fluid from ice crystals can be used during siphoning.

Hydrophilic liquids (ethanol and ethylene glycol) are mixed with water at any concentration. The equilibrium concentration of the aqueous solutions of the hydrophilic liquids is the mass of the solvent containing in the solution at condition of *thermodynamic equilibrium*, a state of system if it is simultaneously in mechanical, thermal and chemical equilibrium. This means that thermodynamic variables (temperature, pressure and thermodynamic potentials) are constant throughout the system.

Equilibrium concentration of aqueous ethanol and ethylene glycol solutions is considered usually as concentration of the solvent at freezing point. Thus, equilibrium concentration of ethanol solutions *versus* temperature [°C] is estimated in the limited range according to linear relation (*Zagorodnov et al*., 1994; *V.Zagorodnov*, personal communication):

$$C_{eq} = -\,0{,}01454t; \tag{3}$$

or

$$C_{eq} = -\,0{,}01334t. \tag{4}$$

Ice solubility

The ice solubility is very important characteristic of the drilling fluid. All liquids can be divided to fluids (a) inert to ice, (b) slightly dissolving ice and (c) active to ice.

There are two polar opinions to the problem of ice solubility by drilling fluids. The first view is that the drilling in ice is possible only with fluids that are inert to the ice, and the second view is that the drilling with active to ice fluids is more advantageous.

It is well known that active fluids dissolve ice or water formed after the destruction or melting of ice at the bottom of the bore-hole, as well, the ice from the bore-hole walls too. The process of dissolving is going up to the equilibrium concentration of the aqueous solution, and after the some time the flush is formed in the bore-hole (this fact was confirmed at Byrd Station, 1969, Novolazarevskaya station, 1972, and some other drilling sites). For our opinion, the drilling with inert fluids is more safety and provides the bore-hole stability of long duration.

The value of ice solubility is measured by tests when the ice samples are put into a cooling fluid in static conditions. It is obviously that the rate of ice weight loss depends on chemical composition of the fluid, the temperature, and the square of the surface if ice that is in contact with fluid. In the references we can find the results of tests with ice samples of cubic or cylindrical forms (the squares of the cube and cylinder are differed and, therefore, it is difficult to compare the results of investigations), but usually the ice cubes are used.

After the definite time the ice samples are weighed carefully and intensity of the ice weight loss is expressed by the absolute rate of dissolving v_W [g/h] or the relative rate of dissolving $\overline{v_W}$ [h^{-1}]:

$$v_W = \frac{dm}{dT}; \tag{5}$$

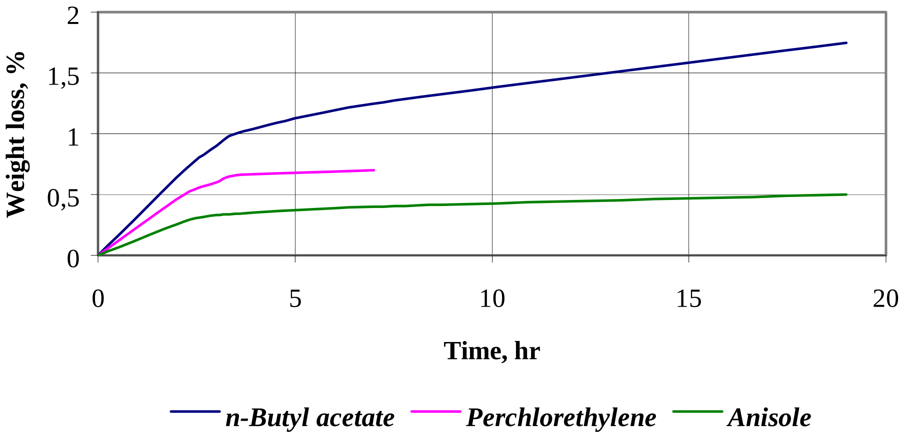
$$\overline{v_W} = \frac{v_W}{T}, \tag{6}$$

where *dm* is the mass-loss of the ice sample during the time *dT* [h], g; *T* is the total time of contact, h.

Hydrophobic liquids are completely inert to ice at negative temperatures: the ice samples don't lose the weight during several days in contact with diesel fuel, fuel TS-1, solvents of Exxol D30 and D60, mixtures of petroleum liquids with densifiers-fluorocarbons (CFC11, HCFC 123, HCFC 141b) (*Pashkevich and Chistyakov*, 1989; *Gosink et al.*, 1989; *P.Talalay*, unpublished). This conclusion is confirmed by experience of ice drilling using fluids of kerosene type with densifier: the stability of ice walls is kept safe during drilling operation, as well as, during many years after drilling.

Fluids slightly dissolving ice (n-butyl acetate, anisole, perchlorethylene) can successfully used as drilling fluids. The function of the ice weight loss in dependence on the time of contact isn't linear (*Fig.1*), the process of dissolving is the most intensive at the first few hours of contact. Then the process is stabilized and finished, when the maximal water solubility is achieved at given temperature. This conclusion is confirmed by tests in which the weight loss of ice sample in n-butyl acetate saturated by water was not noticeable in seven hours contact time (*Gosink et al*., 1989).

Fig.1. The weight loss of ice in drilling fluids at temperature -19 C (Gosink et al., 1989)



Experiments carried out in Copenhagen University showed that 30-g cube of ice lost 0,4 g of its weight in 110 g of cooling n-butyl acetate at temperature –15 °C during 28 hours, and then the ice dissolving stopped. It means that water solubility of n-butyl acetate is about 0,35 % at this temperature.

Hydrophilic liquids are active to ice. The rate of the ice weight loss in hydrophilic liquids and its aqueous solutions is very rapid and it depends on the temperature and on the concentration of the solution (*Table 5*). This type of liquid dissolves ice up to the equilibrium concentration at given temperature. Experimental tests showed that the ice cube with mass 20 g after 2-hour contact with 100 ml of ethanol lost the 76 % of its mass (*Gosink et al*., 1989).

Table 5. The absolute rate of ice dissolving in hydrophilic liquids
(*Shamshev and Yakovlev*, 1973; *Gosink et al.*, 1989)

Liquid	Concentration, % by mass	Temperature, °C	Contact time, h	Rate of dissolving, g/h
Aqueous solution of ethylene glycol	11	-2,5	0,5	1,00
Aqueous solution of ethanol	8,5	-2,5	0,5	0,78
Ethanol	99,9	-19	2,0	7,60

Other kinds of interaction between ice and drilling fluid

The chemical and/or physical interaction between ice and drilling fluids (except the ice solubility) didn't research sufficiently. There are some references about the inertness of oil hydrocarbons with respect to the ice due to screen hydrophobic pellicle that is formed on the surface of ice (*Litvinenko et al.*, 1996).

On the other hand tests with the mixture of Exxon D60 with densifier HCFC 141b (density near 935 kg/m^3 at –15 °C) blended with ice chips showed that after a week of contact the part of ice chips formed a sediment, a part of ice chips was in suspension and a part of ice chips was at the top of the fluid (Fig. 2,a). The whole ice chips blended with the mixture of Exxon D60 with densifier HCFC 123 (the same density near 935 kg/m^3 at –15 °C) were at the top of the fluid (Fig. 2,b). It means that the densifier HCFC 141b influences on the ice such way that the ice chips become heavier.

This fact was confirmed during drilling at North GRIP, Greenland, (*Gundestrup*, 1997) and at Dome C (*J.P.Steffensen*, personal communication). In both cases the drilling fluid was solvent Exxon (Exxon D60 at North GRIP and Exxon D30 at Dome C) with densifier HCFC 141b (density near 930-935 kg/m^3), and in both cases the electromechanical drills of same type were stuck at the depths 1371 m (1997, North GRIP) and 786 m (1998, Dome C). It was noticed that ice chips slowly formed the sediment that probably was one of the causes of the sticking the drill. The chemical/physical interaction between the ice and the densifier HCFC 141b isn't clear.

(a) (b)

Fig.2. Ice chips blended with mixture of (a) Exxol D60 with densifier HCFC 141b and (b) Exxol D60 with densifier HCFC 123 after one week of contact

11. TOXICOLOGICAL AND ENVIRONMENTAL REQUIREMENTS

Standards and recommendations to air contaminants

The choice of the non- or little toxic drilling fluid is one of the main requirements of toxicological and hazard control. Although the drilling sites may be outside of the national boundaries, employers should follow the standards and recommendations of the health safety for all types of workers employed as drillers, scientists, technicians, and support personnel.

There are many national regulations specified by different government agencies or recommendations by expert groups in USA, Germany, Denmark, Russia and other countries (*Table 1*). The most of the limit values specified by these organizations are similar, but some differences exist.

Table 1. Organizations specified workplace air levels and exposure limit marking

Organization		**Exposure limit marking**	
Name	**Abbreviation**	**Name**	**Abbreviation**
Occupational Safety and Healthy Administration (USA)	OSHA	Permissible Exposure Level	PEL
American Conference of Governmental Industrial Hygienists	ACGIH	Threshold Limit Values	TLV
German Research Society	DFG	Maximum Allowable Concentration	MAK
National Institute for Occupational Safety and Health (USA)	NIOSH	Recommended Exposure Level	REL
Factories Inspectorate (Arbejdstilsynet, Denmark)	-	Limit Value (Grænseværdien)	GV
Institute of Labour and Hygienics (Russia)	-	Maximum Permissible Concentration	PDK

Many countries and local administrative agencies throughout the world adopt the ACGIH TLVs in whole or in part. As a result, these recommendations have a major effect on the control of workplace contaminant concentrations. The latest annual TLV list is containing in publication "*Threshold Limit Values and Biological Exposure Indices*".

The workplace air contaminant levels listed at Table 2 shall be avoided, or protective equipment shall be provided and used. The permissible exposure is specified for a normal 8-hour workday, 40-hour workweek, to which nearly all workers may be exposed repeatedly without adverse effect.

Table 2. Permissible exposure of vapor or gas in indoor air of working rooms at temperature 25 °C and pressure 101325 Pa

Fluid	**Hazard rating**	**Workplace air levels**		**References**
		ppm (by vol.)	**mg/m^3**	
		Petroleum oil liquids		
Kerosene	**3**	GV: **100**	-	*Kemikalie-Brugsanvisnings-Seekretariatet* (Chemical Instructions Office); Denmark, 1989
		NIOSH REL: **14**	**100**	*Patty's Industrial Hygiene and Toxicology*, 1981
Solvent Exxol D30, D40, D60	*3*	**100**	**600**	*Producer's data*
		Densifiers		
Trichlorethylene	**3**	GV: **30**	**160**	*Arbejdstilsynets liste over Grænseværdier for stoffer og materialer*, 1984
		OSHA PEL: **50**	-	*Lewis*, 1996
		ACGIH TLV: **50**	-	
		DFG MAK: **50**	**270**	
		NIOSH REL: **250**	-	
Perchlorethylene	**3**	GV: **30**	**200**	*Arbejdstilsynets liste over Grænseværdier for stoffer og materialer*, 1984
		OSHA PEL: **25**	-	*Lewis*, 1996
		ACGIH TLV: **50**	-	
		DFG MAK: **50**	**345**	
CFC 11	**2**	OSHA PEL: **1000**	-	*Lewis*, 1996
		ACGIH TLV: **1000**	-	
		DFG MAK: **1000**	**5600**	
		-	PDK: **5000**	*Promyshlennye hlororganicheskiye soedineniya*,1978
CFC 113	**3**	GV: **500**	**3800**	*Grænseværdier for stoffer og materialer*, 1984
		ACGIH TLV: **1000**	**7600**	*Handbook of Chemistry and Physics*, 1976
HCFC 141b	**1**	**500**	-	*Producer's data*
		Alcohols, esters and other organic liquids		
Ethylene Glycol	**3**	GV: **50**	**130**	*Arbejdstilsynets liste over Grænseværdier for stoffer og materialer*, 1984
		OSHA PEL: **50**	-	*Lewis*, 1996
		ACGIH TLV: **50**	-	
		DFG MAK: **10**	**26**	
Ethanol	**3**	OSHA PEL: **1000**	-	*Lewis*, 1996
		ACGIH TLV: **1000**	-	
		DFG MAK: **1000**	**1900**	
		-	PDK: **1000**	*Litvinenko et al.*, 1996
n-Butyl acetate	**3**	ACGIH TLV: **150**	**710**	*Handbook of Chemistry and Physics*, 1976
		OSHA PEL: **150**		*Lewis*, 1996
		DFG MAK: **200**	**950**	

We have to note that the standards and recommendations for a particular fluid can be changed due to obtaining of new hazard data. To obtain a new data it is necessary to contact with the applicable organization for information about current standards (for example: ACGIH, Kemper Woods Center, 1330 Kemper Meadow Drive, Cincinati, OH 45240 USA).

The hazard rating assigned to each fluid in the form of number (1,2, or 3) and listed in *Table 2* identifies the level of toxicity or hazard according to classification represented below (*Lewis*, 1996).

Table 3. Hazard ratings of dangerous materials

Hazard rating	**Level of hazard**	**Description***
1	Low toxic, fire, explosive, or reactivity hazard	An LD_{50} of 4000 – 40000 mg /kg or an LC_{50} of 500 – 500 ppm; or that material is combustible or has some reactivity hazard
2	Medium toxic, fire, explosive, or reactivity hazard	An LD_{50} of 400 – 4000 mg/kg or an LC_{50} of 100 – 500 ppm; or that the material is flammable or reactive
3	High toxic, fire, explosive, or reactivity hazard	An LD_{50} below 400 mg/kg or an LC_{50} below 100 ppm; or that material is explosive, highly flammable, or highly reactive

*The definition of the exposures LD_{50} and LC_{50} see *Table 4*.

Toxicity dose data of drilling fluids

The exposures used in toxicology have the following classification (Table 4): the dose caused death (LD) or other toxic effects (TD) and whether it is administered as a lethal concentration (LC) or toxic concentration (TC) in inhaled air. In general, the subscript “Lo” is used where the number of subjects studied was not a significant number from the population. The subscript “50” means the lethal dose percentage (the death of 50 % of an entire defined experimental animal population).

Table 4. Description of the exposures used in toxicology (Lewis, 1996)

Category	**Name**	**Exposure time**	**Route of exposure**	**Toxic effect**	
				Human	**Animal**
TD_{Lo}	Toxic Dose Low	Acute or chronic	All except inhalation	Any non-lethal	Carcinogenic, neoplastigenic, tetratogenic, reproductive effects
TC_{Lo}	Toxic Concentration Low	Acute or chronic	Inhalation	Any non-lethal	Carcinogenic, neoplastigenic, tetratogenic, reproductive effects
LD_{Lo}	Lethal Dose Low	Acute or chronic	All except inhalation	Death	Death
LD_{50}	Lethal Dose Fifty	Acute	All except inhalation	Not applicable	Death (statistically determined)
LC_{Lo}	Lethal Concentration Low	Acute or chronic	Inhalation	Death	Death
LC_{50}	Lethal Concentration Fifty	Acute	Inhalation	Not applicable	Death (statistically determined)

Table 5. Toxic effects of drilling fluids to human and animals (Lewis, 1996; producers data)

Name	Category of exposure					
	TD_{Lo}	TC_{Lo}	LD_{Lo}	LD_{50}	LC_{Lo}	LC_{50}
Hydrocarbons						
Diesel fuel				Orl-rat 9g/kg		
Kerosene	Orl-man 3570 mg/kg:P,G; Ivn-man 403 mg/kg:C		Orl-man 500mg/kg; Unr-man 1176 mg/kg; Ipr-rat 10700 mg/kg; Itr-rat 800 mg/kg; Orl-dog 4g7kg; Ivn-dog 200 mg/kg; Itr-dog 800 mg/kg	Orl-rat >5g/kg; Orl-rbt 28 g/kg; Ipr-rbt 6600 mg/kg; Ivn-rbt 180 mg/kg; Itr-rbt 200 mg/kg; Orl-gpg 20 g/kg		Ihl-rat >5g/m^3/4H
Exxol D60				Orl-rat 5g/kg		
Densifiers						
Trichlorethylene	Orl-rat 2688 g/kg:R; Orl-mus 455 g/kg/78W:Cr; Orl-man 2143 mg/kg:G; Ihl-hmn 812 mg/kg:C,G,L	Ihl-rat 100 ppm/4H:T; Ihl-rat 150 ppm/7H/2Y:Cr; Ihl-ham 100 ppm/6H/77W:Et; Ihl-hmn 6900 mg/m^3/10M:C; Ihl-hmn 110 ppm/8H:E,C	Orl-hmn 7g/kg; Scu-dog 150 mg/kg; Ivn-dog 150 mg/kg; Orl-cat 5864 mg/kg; Orl-rbt 7330 mg/kg; Scu-rbt 1800 mg/kg	Orl-rat 5650 mg/kg; Ipr-rat 1282 mg/kg; Orl-mus 2402 mg/kg; Ivn-mus 33900 µg/kg; Ipr_dog 1900 mg/kg	Ihl-gpg 37200 ppm/40M	Ihl-rat 25700 ppm/1H; Ihl-mus 8450 ppm/4H
Perchlorethylene	Orl-mus 195g/kg/50W:Cr; Orl-cld 545 mg/kg:C	Ihl-rat 900 ppm/7H:R; Ihl-rat 1000 ppm/24H:T; Ihl-rat 200 ppm/6H/2Y:Cr; Ihl-hmn 96 ppm/7H:Pn,E,C; Ihl-man 600 ppm/10M:E,C	Ihl-man 2857 mg/kg; Orl-dog 4000 mg/kg; Ivn-dog 85 mg/kg; Orl-cat 4000 mg/kg	Orl-rat 2629 mg/kg; Ipr-rat 4678 mg/kg; Orl-mus 8100 mg/kg; Scu-mus 65 g/kg; Ipr-dog 2100 mg/kg		Ihl-rat 34200 mg/m^3/8H; Ihl-mus 5200 ppm/4H;
CFC 11	Ihl-hmn 50000 ppm/ 30 M:E,P,L			Ipr-mus 1743 mg/kg	Ihl-rat 10 pph/30M	Ihl-mus 10 pph/30 M; Ihl-rbt 25 pph/30 M; Ihl-gpg 25 pph/30M

Table 5. (continued)

Name	**Category of exposure**					
	TD$_{Lo}$	**TC$_{Lo}$**	**LD$_{Lo}$**	**LD$_{50}$**	**LC$_{Lo}$**	**LC$_{50}$**
CFC 113				Ipr-mus 8600 mg/kg		Ihl-rat 13 pph/15M
HCFC 123						Ihl-mus 74000 ppm/1H
HCFC 141b				Ihl-rat 240 g/m^3/2H; Orl-rat >5 g/kg		Ihl-mus 151 g/m^3/2H; Ihl-rat 62300 ppm/4H
HCFC 225				Orl-rat >5g/kg		Ihl-rat 37000 ppm/4H
Alcohols and esters						
Ethylene glycol	Orl-mus 84 g/kg:R; Orl-rat 8580 mg/kg:T; Orl-rat 25g/kg:R; Orl-rat 50 g/kg:T; Orl-chd 5500mg/kg:C,G,K	Ihl-hmn 10000 mg/m^3:E,P	Orl-hmn 786 mg/kg; Unr-man 1637 mg/kg; Ims-rat 3300 mg/kg; Scu-mus 2700 mg/kg	Orl-rat 4700 mg/kg; Ipr-rat 5010 mg/kg; Scu-rat 2800 mg/kg; Ivn-rat 3260 mg/kg; Orl-mus 7500 mg/kg; Ipr-mus 5614 mg/kg		
Ethanol	Orl-wmn 41 g/kg:R; Iut-wmn 200 mg/kg:R; Ipr-rat 15 g/kg:R; Orl-gpg 90 g/kg:R; Orl-rat 132 g/kg:R; Orl-dog 21,6 g/kg:R; Orl-man 50 mg/kg:G		Orl-chd 2000 mg/kg; Orl-dog 5500 mg/kg; Ipr-dog 3000 mg/kg; Scu-dog 6000 mg/kg	Orl-rat 7060 mg/kg; Ipr-rat 3750 mg/kg; Ivn-rat 1440 mg/kg; Orl-mus 3450 mg/kg; Ipr-mus 933 mg/kg; Scu-mus 8285 mg/kg; Ivn-mus 1973mg/kg		Ihl-rat 20000 ppm/10H; Ihl-mus 39 g/m^3/4H
n-Butyl acetate		Ihl-rat 1500 ppm/7H:T; Ihl-hmn 200 ppm:N,E,P	Orl-gpg 4700 mg/kg; Ipr-gpg 1500 mg/kg	Orl-rat 13100 mg/kg; Orl-mus 1060 mg/kg; Ipr-mus 1230 mg/kg; Orl-rbt 3200 mg/kg	Ihl-cat 68 g/m^3/72M; Ihl-gpg 67 g/m^3/4H	Ihl-rat 2000 ppm/4H; Ihl-mus 6 g/m^3/2H
Anisole				Orl-rat 3700 mg/kg; Orl-mus 2800 mg/kg		Ihl-mus 3021 mg/m^3/2H;

The toxicity dose data listed in *Table 5* include:

- route of exposure;
- species of animal studied;
- amount of material per body weight or concentration per unit of air volume;
- duration of exposure, where it is available;
- toxic effects (for TD_{Lo} and TC_{Lo}).

The toxicological results of studies on rats or mice are the most frequently reported and hence provide the most useful data for comparative purposes. The term abbreviations are given in *Table 6.*

Table 6. The abbreviations and definitions of various routs, species, duration of exposure and toxic effects

Abbreviation	**Definition**
Route of exposure	
Ihl	Inhalation in chamber, by cannulation, or through mask
Ims	Intramuscular: administration into the muscule by hypodermic needle
Ipr	Intraperitonel: administration into the peritoneal cavity
Itr	Intratracheal: administration into the trachea
Iut	Intrauterine: administration into the uterus
Ivn	Intravenous: administration directly into the vein by hypodermic needle
Orl	Oral: per os, intragastric, feeding, or introduction with drinking water
Scu	Subcutaneous: administration under the skin
Unr	Unreported: route doesn't specified in the reference
Species (age)	
cat	Cat (adult)
chd	Child (1-13 years)
dog	Dog (adult, 52 weeks)
gpg	Guinea Pig (adult)
ham	Hamster (14 weeks)
hmn	Human (adult)
man	Man (adult)
mus	Mouse (8 weeks)
rat	Rat (adult, 14 weeks)
rbt	Rabbit (adult, 12 weeks)
wmn	Woman (adult)
Available duration of exposure	
M	Minutes
H	Hours
D	Days
Y	Years
Toxic effects	
C	Central nervous system effects (headaches, tremor, drowsiness, convulsions, hypnosis, anesthesia)
Cr	Carcinogenic effects
E	Eye effects (irritation, diplopia, cataracts, eye ground, blindness)
Et	Equivocal tumorigenic agent

G	Gastrointestinal tract effects (diarrhea, constipation, ulceration)
K	Kidney effects
L	Liver effects
N	Nose effects
P	Pulmonary effects (effects on respiration and respiratory pathology)
Pn	Peripheral nervous system effects
R	Reproductive effects
T	Teratogenic effects (non-transmissible changes produced in the off-spring)

Skin and eye irritation

In the dependence of skin and eye reaction the dangerous materials are divided to:

- corrosive materials (corrosive effects – burns, desquamation, for example, concentrated sulfuric acid);
- allergens (allergic systematic reaction of an acute or chronic nature);
- irritants (local skin and eye effects, more properly termed as “primary irritation”).

A primary irritant is a material that, if present in sufficient quantity for a sufficient period of time, will produce a non-corrosive and a non-allergic reaction of the skin and eye. The most widespread animal irritation test is the *Draize* procedure applied to the skin and the eye of albino rabbits (the description see “*Journal of Pharmacology and Experimental Therapeutics*”, Vol. 82, 1944, p. 377-419). The *Draize* procedure has become the standard test specified by the government of USA (*Lewis*, 1996).

In the case of the positive test results three rating of the skin irritation are used: **mild** (well-defined erythema and slight edema), **moderate** (moderate-to-serve erythema and moderate edema), or **severe** (severe erythema to slight eschar formation and severe edema). Fluids producing any degree of irritation are identified as irritants. Skin and eye irritation data on rabbits (*Table 7*) include:

- dose amount of irritant (in *milligrams*);
- exposure time (in *hours*).

Table 7. Irritant effect of drilling fluids

Name	Administration directly onto to the surface of the eye		Application directly onto the skin	
	Exposure	Reaction	Exposure	Reaction
Diesel fuel	-	-	500 mg/72H	moderate
Kerosene	-	-	500 mg/72H	severe
Trichlorethylene	20 mg/24H	moderate	500 mg/24H	severe
Perchlorethylene	500 mg/24H	mild	810 mg/24H	severe
Ethylene glycol	100 mg/1H 1440 mg/6H	mild moderate	555 mg/72H	mild
Ethanol	100 mg/24H 500 mg/24H	mild moderate	20 mg/24H 500 mg/24H	moderate severe
n-Butyl acetate	20 mg/72H	severe	500 mg/24H	moderate
Anisole	-	-	500 mg/24H	moderate

Comments to toxic and irritant properties of drilling fluids

Diesel fuel causes a mildly toxic effect by ingestion. It is a moderate skin irritant. Carcinogenic effect of diesel fuel is questionable. When it is heated to decomposition it emits acrid smoke and irritating vapors.

Kerosene (*Selected petroleum products*, 1982) is the suspected carcinogenic material. Human systematic effects by ingestion and intravenous routs: somnolence, hallucinations and distorted perceptions, coughing, nausea or vomiting, and fever.

Kerosene is not sufficiently volatile to constitute an acute inhalation hazard, except when it is emitted as an aerosol or mist, kerosene may cause muscous membrane irritation and chemical pneumonitis, particularly in young children. For mixtures containing 43% or more kerosene, the aspiration hazard is acute.

It is a severe skin irritant: contacts with skin may lead to irritation, infection, and dermatitis. Kerosene is not irritant to eye.

When it is heated to decomposition it emits acrid smoke and fumes.

Jet fuels have the physiological effects resemble those of kerosene, however in addition, neurological effects have been recorded (*Patty's Industrial Hygiene and Toxicology*, 1981).

Trichlorethylene is the suspected carcinogenic material (*Trichloroethylene*, 1985). Trichlorethylene has experimental reproductive effects, and the human mutation data is reported. There is a damage to liver and other organs from chronic exposure.

Human systematic effects by ingestion and inhalation: eye effects, somnolence, hallucinations, or distorted perceptions, gastrointestinal changes, and jaundice. Prolonged inhalation of moderate concentration causes headache and drowsiness, inhalation of high concentrations causes narcosis and anesthesia.

It is an eye and severe skin irritant.

Table 8. Effects of drilling fluids to human health according to recommendations of Kemikalie-Brugsanvisnings-Seekretariatet (Chemical Instructions Office); Denmark, 1989

Fluids	**Effects to human health***							
	Carcinogenic effects	**Reproductive effects**	**Mutation effects**	**Skin allergy**	**Allergic asthma**	**Nervous system effects**	**Lung, liver, kidney effects**	**Other effects**
Kerosene	2	2	4	3	4	3	4	4
Perchlorethylene	2	2	3	3	4	3	3	4
CFC 113	4	4	4	3	4	3	2	4
n-Butyl acetate	4	4	4	3	4	3	4	4
Anisole	4	4	4	4	4	3	3	4

*1 – no; 2 – suspected; 3 – yes; 4 – no documentation

Perchlorethylene (*Tetrachloroethylene*, 1984) is the confirmed carcinogenic, neoplastigenic, and teratogenic material. Trichlorethylene has experimental reproductive effects, and the human mutation data is reported. The symptoms of acute intoxication from perchlorethylene are the result of its effects upon nervous system.

Prolonged inhalation of moderate concentration causes local anesthetic, conjunctiva irritation, general anesthesia, hallucinations, distorted perceptions, coma, and pulmonary changes.

It is an eye and severe skin irritant. The liquid can cause injuries to the eyes, and after repeated or prolonged contact with skin it can cause dermatitis.

When it is heated to decomposition it emits highly toxic fumes of Cl^-.

Fluorocarbons were introduced in the 1940s, and they were regarding as inert harmless agents, but then the toxicological data became apparent that fluorocarbons are not inert and that they are slightly or moderately toxic by ingestion and inhalation. Most fluorocarbons have similar patterns of toxicity and have interchangeable uses (*Fully halogenated chlorofluorocarbons*, 1990; *Partially halogenated chlorofluorocarbons*, 1992).

At high levels of concentration fluorocarbons cause adrenaline to sensitize the heart, so that arrhythmia may develop. Long-term exposure to high concentrations of this class of chemicals may cause adverse effects on the liver, nervous system, and reproduction development. The sensory threshold level of fluorocarbons is from 5000 to 10000 ppm.

When fluorocarbons are heated to decomposition they emit very toxic vapors of F^- and Cl^-.

Trichlorofluoromethan CFC 11 in high concentrations causes narcosis and anesthesia in humans. Human systematic effects by inhalation: conjunctiva irritation, fibrosing alveolitis, and liver changes. CFC 11 is not irritating to the skin and lightly irritant to the eyes.

Trichlorotrifluoroethane CFC 113 is a moderately toxic by inhalation. CFC 113 has the physiological effects resemble those of CFC 11. In man no unwanted effects were seen in 50 worker exposed from 46 to 4700 ppm for an average duration of 2,77 years.

Dichlorotrifluoroethane HCFC 123 is a moderately toxic by inhalation. Inhalation of high concentrations causes feelings of intoxication, restlessness, dizziness, and drowsiness. Human systematic effects by inhalation: cardiac arrhythmia and asphyxia by lack of oxygen.

It is an eye and skin moderate irritant. In the case of eye contact it can cause the temporary eye lesions, in the case of repeated contact with skin it causes dry and chapped skin.

Dichlorofluoroethane HCFC 141b is a slightly toxic by inhalation. No adverse reproductive effect was found in two-generation reproduction study with exposure levels of up to 20000 ppm. HCFC 141b is not irritating to the skin and lightly irritant to the eyes.

Dichloropentafluoropropan HCFC 225ca/cb is an eye and skin moderate irritant. Exposure to very high vapor concentrations can induce toxicity from giddiness, weakness, dizziness, nausea, to unconsciousness. Water is incompatible material with HCFC 225ca/cb: long term contact with water can deplete stabilizers followed by slow hydrolysis, which produces composite acids.

Ethylene glycol is the confirmed teratogenic material. It is a moderately toxic by ingestion (lethal dose for humans reported to be 100 ml) and a very toxic in particulate form upon inhalation. Ethylene glycol has experimental reproductive effects, and the human mutation data is reported.

Human systematic effects by ingestion and inhalation: eye lacrimation, general anesthesia, headache, cough, respiratory stimulation, nausea or vomiting, pulmonary, kidney, and liver changes.

It is a skin, eye, and mucous membrane irritant.

When ethylene glycol is heated to decomposition it emits acrid smoke and irritating fumes.

Ethanol is the confirmed carcinogenic, tumorigenic and teratogenic material. It is a moderately toxic by ingestion and mildly toxic by inhalation and skin contact. Ethanol has experimental reproductive effects, and the human mutation data is reported.

Human systematic effects by ingestion: sleep disorders, hallucinations, distorted perceptions, convulsions, motor activity changes, ataxia, coma, antipsychotic, headache, pulmonary and gastrointestinal changes.

Exposure to concentration over than recommended threshold limit (1000 ppm) may cause headache, irritation of eyes, nose, and throat, and, if continued for an hour, drowsiness and lassitude, loss of appetite, and inability to concentrate.

Ethanol is an eye and skin irritant.

n-Butyl acetate is the confirmed teratogenic material; it is a mildly toxic by inhalation and ingestion.

Butyl acetate odors are detectable at 10 ppm. Human systematic effects by inhalation: conjunctiva irritation, unspecified nasal and respiratory system effects.

Butyl acetate is a skin and severe eye irritant and a mild allergen. A mild irritation of the nose and eyes of human has been reported after a few minutes (3-5 min) exposure to 300 ppm, and a strong irritation of nose and eyes – after exposure to 6100 ppm during 13 hrs. High vapor concentrations of n-butyl acetate cause narcosis.

When butyl acetate is heated to decomposition it emits acrid and irritating fumes.

Anisole is a moderately toxic by ingestion and inhalation, and it is a mild skin irritant, but no permissible limit values have been set. Anisole odors are detectable at 0,2 ppm, that is why anisole having a sweet anise-like odor is widely used in perfumery.

When it is heated to decomposition it emits acrid fumes.

Silicon oils of KF96 type are generally harmless to man or animals (*Prospectus* of Shin-Etsu Chemical Co.). If silicon oil comes in contact with eyes, it cause temporary irritation but without permanent harm. Inertness of silicon oils renders these fluids acceptable for use as ingredients of cosmetics, the prevention of human skin from chafing and as defoamers for food and beverages.

Industrial hygiene of drilling fluids using

General consideration.

a) *Air in drilling shelter*. All drilling fluids have the permissible limits of air contaminant (see Table 2), and, therefore, the special attention must be paid to ventilation of working areas and/or to using of a means like vapor-traps. During drilling operations the daily control of air pollution should be organized.

For the decreasing of health hazard from the evaporation of drilling fluid the temperature inside drilling shelter should be not very high, and drilling fluid itself cannot be heated to decomposition because most of them emit toxic vapors.

b) *Cloth*. Almost all drilling fluids are eye and skin irritants. The open areas of skin should be carefully protected. It should be a standard operating procedure for drill operators to change into and out of work in the special cloak-room that must be heated, have an area for the airing and drying of soaked clothing, provide storage area, and must be properly ventilated.

Kerosene types fluids. The odor threshold of kerosene has been estimated at 0,09 ppm (0,6 mg/m^3). The recommended threshold limit value (NIOSN) is 14 ppm (100 mg/m3), which is also the action level. The sensory threshold is 20 ppm (140 mg/m^3) (*Patty's Industrial Hygiene and Toxicology*, 1981). Kerosene vapors can be collected by charcoal absorption.

When kerosene is handled, prolonged skin contact should be avoided, although the surface should be thoroughly washed in case of accidental contact. Kerosene should never be siphoned by mouth.

Perchlorethylene and trichlorethylene have a rather high toxicity. Their use demands especially strong measures to securing of permissible air contaminant in working area, as well as, to the personal protection; they can be safely handled with proper precautions only.

Fluorocarbons are of very low acute toxicity by both inhalation and oral routes. In case of eye or skin contact it is necessary to wash affected areas thoroughly with plenty of water. The eyes should be flushed during at least 15 minutes. Epinephrine or similar medicine can not be used immediately after exposure, because cardiac arrhythmia, including ventricular fibrillation, may occur.

Ethylene glycol is a very toxic material (threshold limit value recommended by German Research Society is 10 ppm only). Therefore, it isn't recommended for use at open working rooms, or it can be safely handled with very strong precautions.

Ethanol has good personal safe properties. Concentrations below permissible limit (1000 ppm) usually produce no signs of intoxication. Though ethanol posses narcotic properties, concentrations sufficient to produce this effect usually are not reached in industry. In case of eye or skin contact it is necessary to wash affected areas thoroughly with plenty of water.

n-Butyl acetate. The main hazard comes from inhaling vapors in excessive concentrations. It cannot be used without sufficient ventilation and/or special means to minimize air pollution.

Field-test results from GISP2 drilling (*Gosink et al.*, 1991) showed that the vapors of n-butyl acetate in the drilling shelter didn't exceed the permissible limit (100 ppm): near the bore-hole mouth vapor concentration went as high as 40 ppm and in the rest of the shelter it was less than 10 ppm. In spite of this measurements the personal communications of PICO drillers showed that after the day-work in the drilling shelter workers felt damages of the central nervous system (dizziness, headaches).

Silicon oils. No special precautions are necessary.

Environmental requirements and properties of drilling fluids

General environmental requirements:

1. Non-toxic or little toxic fluid with good environmental properties should be chosen and used.
2. The drums used for transportation, storage and preparation of drilling fluids should be protected from any kinds of leaks.
3. During drilling the upper permeable part of the glacier should be carefully isolated by casing.
4. The drilling fluid should be recycled, separating liquid and ice chips in a filter.
5. The ice chips should be collected in the drums (empty drums from the utilizing fluid can be used).

Kerosene is a high environmental risk material since, in the event of a spill, it has a long residence time, particularly in cold environment. The most hazard hydrocarbons are aromatics that are the compounds of the almost all petroleum oil products. In the water environmental the concentrations of aromatics more than 1 mg/m^3 cause the poison effects to microorganisms (*Talalay and Chistiyakov*, 1998).

The maximum concentration of aromatics in turbine fuels is 20 – 25 %, and in solvents of Exxol D type – 0,5 % only. Therefore, solvents of Exxol D type are the best of kerosene type oil hydrocarbons from an environmental consideration.

Perchlorethylene is difficult to biodegrade. This material is extremely stable and resists hydrolysis.

Fluorocarbons. In 1974, *M.J.Molina* and *F.S.Rowland* drew attention to a potential biologic hazard resulting from depletion of the ozone layer owing to release of fluorocarbons into atmosphere. A reduction in the ozone allows more ultraviolet light to reach the earth’s surface and is anticipated to increase the incidence of malignant melanoma, a serious form of skin cancer frequently causing death, and increase incidence of basal and squamous-cell carcinomas of the skin that are less serious but more prevalent.

Non-hydrogenated fluorocarbons (CFC 11, CFC 113, CFC 12 and others) are more stable in the atmosphere and are more dangerous for ozone layer than hydrogenated fluorocarbons (HCFC 123, HCFC 141b, HCFC 225 and others): the hydrogen-containing fluorocarbons have lifetimes about 5 to 100 times shorter than those for all non-hydrogenated.

Protocols signed by the most of the world countries in Montreal (1987) and in London (1990) ordered to reduce the production of the dangerous fluorocarbons up to 50% since 1995 and to stop the production of such fluorocarbons since 2000. The most dangerous non-hydrogenated fluorocarbons CFC 11 and CFC 113 are not aloud for use after 1995. The use of hydrogenated fluorocarbons is limited to a transition period, and they will be phased out in 2030 (Copenhagen, 1992).

The widespread characteristics of environmental hazard of fluorocarbons and some other materials are (*Table 9*):

a) for effect on stratospheric ozone - Ozone Depletion Potential (ODP) based on UNEP/WMO Scientific Assessment (1991) [$\text{ODP}_{\text{CFC 11}} = 1$];
b) for greenhouse effect - Global Warming Potential (GWP) calculated from UNEP Scientific Report (1991) [$\text{GWP}_{\text{CFC 11}} = 1$].

Table 9. Environmental properties of fluorocarbons

Name	Atmospheric lifetime, years	ODP	GWP
CFC 11	100	1	1
CFC 113	100	1,07	1,4
HCFC 123	1,7	0,02	0,022
HCFC 141b	9,4	0,11	0,09
HCFC 225ca	2,7	0,025	0,04

HCFC 245fa	7,4	0	0,18
HCFC 365mfc	10,8	0	0,18

n-Butyl acetate has quite good biodegrading properties. The evaporation rate of n-butyl acetate is high, and therefore, if n-butyl acetate will be leaked out, most of it should rather rapidly evaporate.

Ethanol is easily biodegradable, natural, widely occurring product. It would be rapidly consumed by the microbiota in any water body into which it might be spilled, and its infinite solubility would assure its dispersion.

Silicon oils are absolutely safety to an environment. They are produced from the white silica rocks, otherwise known as sand. Silicon – the main component of silicon oils – is the second most common element in the Earth’s crust, after No 1, oxygen. Silicon oils of KF96 type are harmless to microorganisms and animals.

12. COST

The final choice of the drilling fluid depends on the rational correlation between the cost of drilling fluid and other properties of the fluid (generally, density-viscosity properties and, as well as, toxicological and environmental properties). One of the main considerations of the n-butyl acetate use by US specialists (*Gosink et al*., 1989) and Japanese drillers was the low price of this fluid in spite of rather high health hazard.

The expenses for the purchase and for the delivery of drilling fluid are one of the main parts of the total cost of the drilling project. The considerable cost for the use of drilling fluid comes not from the purchase, but from its transportation to the remote polar sites. The cost of transportation to Greenland or Antarctica is estimated about 3 to 4 USD per kg (*Gosink et al*., 1994).

The cost of the some components of drilling fluids and mixtures are listed at *Table 1*. We try to convert national currency to USD but the price of drilling fluid in USD is not very accurate because of the changing of exchange rate. We have to note that the price of the majority of fluids is reduced in time because of the expansion and improving of its manufacture. It is concerned especially to densifiers – fluorocarbons.

The cost of other fluids is decreased too. For example, the cost of silicon oil KF96-1,5cs was near 40 USD per kg in 1993 (it was one of the reason of the refusing of its use by Japanese drillers) and it is near 8 USD per kg now.

Distributor costs of drilling fluid is a little higher than listed at *Table 1* because of the additional price of barrels or drums for transportation.

Table 1. The cost of drilling fluids

Name	**Price in units of reference***		**Price in USD***		**References**
	per *kg*	**per *l***	**per *kg***	**per *l***	
Petroleum oil liquids					
Fuel DF-A	4,6 DKK	3,7 DKK	0,69	0,55	*Cost of distribution in Greenland*
Fuel Jet A1	4,7 DKK	3,8 DKK	0,70	0,57	*Cost of distribution in Greenland*
Exxol D60	4,1 FRF	3,2 FRF	0,72	0,57	*Producer's data*
Exxol D30	4,2 FRF	3,2 FRF	0,75	0,57	*Producer's data*
Densifiers					
Perchlorethylene**	75 DKK	122 DKK	11,3	18,3	(quantity 10 *l*) Stuers Kebo Lab.
Trichlorethylene **	83 DKK	122 DKK	12,5	18,3	(quantity 10 *l*) Stuers Kebo Lab.

HCFC 123	103,5 FRF	153,1 FRF	18,5	27,4	*Producer's data*
HCFC 141b	21,8 FRF	26,8 FRF	3,9	4,8	*Producer's data*
HCFC 225ca	193,5 FRF	300 FRF	34,7	53,7	*EPICA Drilling Group,* 1994
Mixtures					
Exxol D60 + 25 % HCFC 123	-	25,7 FRF	-	4,5	*Calculation*
Exxol D60 + 31,7 % HCFC 141b	-	8,6 FRF	-	1,5	*Calculation*
Exxol D30 + 27,6 % HCFC 123	-	27,6 FRF	-	4,9	*Calculation*
Exxol D30 + 34,2 % HCFC 141b	-	8,9 FRF	-	1,6	*Calculation*
Alcohols, esters and other organic liquids					
Ethylene glycol	10,7 DKK	12 DKK	1,6	1,8	*Mobil DK*
Ethanol **	59,5 DKK	47 DKK	8,9	7,1	(quantity 180 *l*) Stuers Kebo Lab.
n-Butyl acetate	-	-	0,9	0,8	*Gosink et al.*, 1989
Anisole	-	-	~2	~2	*Gosink et al.*, 1989
Silicon oils					
KF96-1,5cs	5000 JPY	4250 JPY	43,2	36,7	*Fujita et al*., 1994
KF96-2,0cs	14 NLG	12,2 NLG	7,5	6,5	*Producer's data*, 1998

* DKK – Danish Kroner;
FRF – France Francs;
JPY – Japan Yen;
NLG – Netherlands Guilders;
USD – United States Dollars

**Cost of the small quantity for chemical purposes (wholesale cost is less in 3-4 times)

CONCLUSIONS

The properties of the potential fluids for deep ice core drilling in Central Antarctica and Greenland are generalized in *Tables 1* and *2*. These tables indicate that there are no ideal drilling fluid, all types of potential drilling fluids have their own advantages and disadvantages. The following considerations emphasize the disadvantages of drilling fluids.

Solvents Exxol D30 and D60 are rather dangerous for the human health: they are severe skin irritants and permissible exposure of vapours in indoor air of working rooms is 100 ppm only. The use of Exxol D30 rises the fire-safety questions, and the use of Exxol D60 rises problems with respect to its relatively low volatility (rate of vaporization is equal to 0,04 of n-butyl acetate rate). From environmental aspect, solvents Exxol D30 and D60 are difficult to biodegrade.

Although the ozone depletion potential of the hydrogenated fluorocarbons (HCFC 123, HCFC 141b, HCFC 225) is less than the potential of non-hydrogenated fluorocarbons (CFC 11, CFC 113), the hazard to ozone layer of atmosphere still remains. This type of the fluid is aggressive to the most types of elastomers, and, moreover, the presence of densifier HCFC 141b cause the inexplicable sedimentation of ice chips in bore-hole. Densifiers HCFC 123 and HCFC 225 had never been used in ice core drilling and, therefore, *in situ* using can bring some new “surprises”.

The main problem of n-butyl acetate use as drilling fluid is hazard to the physical and mental health of the people who work at the coring site. It is impossible to use n-butyl acetate without sufficient ventilation and some means of removing the n-butyl acetate vapors. Personal communications of PICO drillers showed that after the day-work in the drilling shelter workers felt damages of the central nervous system (dizziness, headaches). n-Butyl acetate is very aggressive solvent: there are no elastomers that can able operate in n-butyl acetate during long time. Moreover, the fire hazard of n-butyl acetate is very high: flash point is 22 °C only.

Probably one of the most promising types of the drilling fluid are low-temperature silicon oils. They are non-aggressive, inert, and non-toxic. The main problem of the silicon oils use is their relatively high viscosity at negative temperatures that has influence on the travel time of the drill string and finally on the total time drilling. To achieve the rational free drill’s lowering rate the clearance between drill and bore-hole walls should be increased.

The final choice of the drilling fluid depends on the possibilities and the ways of solving of foregoing problems.

Table 1. Potential drilling fluids for ice core drilling in Central Antarctica (minimal temperatures –60/-50 ℃)

Properties	**Mixture Exxol D30 + HCFC141b**		**Mixture Exxol D30 + HCFC123**		**n-Butyl Acetate**		**Silicon oil KF96-1,5cs**	
	Advantages	**Disadvantages**	**Advantages**	**Disadvantages**	**Advantages**	**Disadvantages**	**Advantages**	**Disadvantages**
Density	Controlled density (at –50 °C): ρ_{D30} = 803 kg/m^3; ρ_{F141b}=1367 kg/m^3		Controlled density (at –50 °C): ρ_{D30} = 803 kg/m^3; ρ_{F123} =1638 kg/m^3		Suitable density: 950 kg/m^3 at –50 °C		Suitable density: 923 kg/m^3 at –50 °C	
Viscosity	Low viscosity (at –50 °C): ν_{D30} = 3,5 cSt; ν_{F141b} = 0,64 cSt		Low viscosity (at –50 °C): ν_{D30} = 3,5 cSt; ν_{F123} ~ 0,8 cSt		Low viscosity: 2,9 cSt at –50 °C			High viscosity: appr. 10 cSt at –50 °C
Frost-resistance	Low freez. point: t_{D30} < -55 °C; t_{F141b} = -103,5 °C		Low freez. point: t_{D30} < -55 °C; t_{F123} = -107 °C		Low freezing point: -78 °C		Low pour point: -76 °C	
Compatibility with polymers and metals		F141b is aggressive to the most elastomers		F123 is aggressive to the most elastomers		Very aggressive solvent	Non-aggressive	
Volatility	Very high rate of vaporization		Very high rate of vaporization		High rate of vaporization			Very low rate of vaporization
Flammability	HCFC 141b is non-flammable	D30 is flammable liquid: flash point is 28 °C	HCFC 123 is non-flammable	D30 is flammable liquid: flash point is 28 °C		Flammable liquid: flash point is 22 °C	Flash point: min 50 °C	
Ice solubility		Ice chips form sediment	Inert			Slightly dissolving of ice	Inert	
Toxicity	TLV$_{F141b}$=500 ppm	TLV$_{D30}$ = 100 ppm	TLV$_{F123}$ = 500 - 1000 ppm	TLV$_{D30}$ = 100 ppm		TLV = 150 ppm	Non-toxic	
Environmental properties		D30 is difficult to biodegrade; ODP$_{F141b}$ = 0,11	ODP$_{F123}$ = 0,02	D30 is difficult to biodegrade	Easy biodegrading		Harmless to environment	
Cost per *liter*	1,6 USD (C_M = 34,2 %)			4,9 USD (C_M = 27,6 %)	0,8 USD			appr. 6,5 USD

Table 2. Potential drilling fluids for deep ice core drilling in Greenland (minimal temperatures near –30 °C)

Properties	**Mixture Exxol D60 + HCFC141b**		**Mixture Exxol D60 + HCFC123**		**n-Butyl Acetate**		**Silicon oil KF96-2,0cs**	
	Advantages	**Disadvantages**	**Advantages**	**Disadvantages**	**Advantages**	**Disadvantages**	**Advantages**	**Disadvantages**
Density	Controlled density (at –30 °C): ρ_{D60} = 821 kg/m^3; ρ_{F141b}=1333 kg/m^3		Controlled density (at –30 °C): ρ_{D60} = 821 kg/m^3; ρ_{F123} =1594 kg/m^3		Suitable density: 930 kg/m^3 at –30 °C		Suitable density: 924 kg/m^3 at –30 °C	
Viscosity	Low viscosity (at –30 °C): ν_{D60} = 4,6 cSt; ν_{F141b} = 0,52 cSt		Low viscosity (at –30 °C): ν_{D60} = 4,6 cSt; ν_{F123} ~ 0,65 cSt		Low viscosity: 1,8 cSt at –30 °C			High viscosity: 5,8 cSt at –30 °C
Frost-resistance	Low freez. point: t_{D60} = -57 °C; t_{F141b} = -103,5 °C		Low freez. point: t_{D60} = -57 °C; t_{F123} = -107 °C		Low freezing point: -78 °C		Low pour point: -84 °C	
Compatibility with polymers and metals		F141b is aggressive to the most elastomers		F123 is aggressive to the most elastomers		Very aggressive solvent	Non-aggressive	
Volatility	F141b has very high rate of vaporization	D60 has low rate of vaporization	F123 has very high rate of vaporization	D60 has low rate of vaporization	High rate of vaporization			Very low rate of vaporization
Flammability	HCFC 141b is non-flammable; flash point of D60: 62 °C		HCFC 123 is non-flammable; flash point of D60: 62 °C			Flammable liquid: flash point is 22 °C	Flash point: min 75 °C	
Ice solubility		Ice chips form sediment	Inert			Slightly dissolving of ice	Inert	
Toxicity	TLV$_{F141b}$=500 ppm	TLV$_{D60}$ = 100 ppm	TLV$_{F123}$ = 500 - 1000 ppm	TLV$_{D60}$ = 100 ppm		TLV = 150 ppm	Non-toxic	
Environmental properties		D60 is difficult to biodegrade; ODP$_{F141b}$ = 0,11	ODP$_{F123}$ = 0,02	D60 is difficult to biodegrade	Easy biodegrading		Harmless to environment	
Cost per *liter*	1,5 USD (C_M = 31,7 %)			4,5 USD (C_M = 25,0 %)	0,8 USD			6,5 USD

ACKNOWLEDGMENTS

We would like to thank Shin-Etsu Co. and Solvay Fluor und Derivate Co. for data regarding to properties of silicon oils and fluorocarbons. The authors thank also Shuji Fujita, Victor Zagorodnov, and Valery Chistyakov for fruitful discussions.

This work is supported by grant of Danish Rectors Scholarship StudID No 4555.

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