DRILLING FLUID OBSERVATIONS AND RECOMMENDATIONS FOR U.S. POLAR PROGRAM, WAISCORES DRILLING PROJECT

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Abstract

Boring ice to depths in excess of about 300 meters requires a fluid with a density closely matched to that of ice to prevent lithostatic pressure from causing plastic collapse of the borehole; the latter frequently results in loss of the drilling equipment. The fluid, or mixture of fluids, must simultaneously satisfy criteria for density, low viscosity, frost resistance, as well as workplace safety and environmental compliance over both the short term (e.g., fire hazard and acute toxicity) and long term (chronic toxicity, local and global environmental degradation). The fluid must also satisfy other criteria, for example those stemming from the analytical methods employed on the ice core.

A number of different fluids and fluid combinations have been tried in the past. Since GISP2 (1990-1993) the US Polar Program has utilized a single-component fluid system, n-butyl acetate, but the toxicology, flammability, aggressive solvent nature, and long-term liabilities of n-butyl acetate raises serious questions about its continued application. The European community, including the Russian program, has concentrated on the use of two-component drilling fluid consisting of low-density hydrocarbon base boosted to the density of ice by addition of halogenated-hydrocarbon (*s.l.*) densifier. Many of the proven densifier products are now considered too toxic, or are no longer available due to efforts to enforce the Montreal Protocol on ozone-depleting substances.

A number of compounds suggested as replacements for ozone-depleting substances such as HCFC's were investigated. Most of these are unsuitable to ice drilling applications and can be dismissed out-of-hand due to toxicity, flammability, unsuitable density, and so forth.

Alternatives categorized as hydrofluorocarbons (HFC's) and hydrofluoroethers (HFE's), may prove to exceed the engineering performance of the now-obsolete densifiers: simultaneously providing high density, low viscosity, materials compatibility, very low toxicity, high safety, convenience in handling, and low environmental liability.

Detailed engineering-related testing tailored to our application would begin by procuring large samples of each compound, as soon as practical. Following a preliminary set of engineering tests to assure ice and drill-materials compatibility, samples of fluid would be supplied to the science community for compliance testing in their analytical streams.

Because both HFC's and HFE's evaporate cleanly, and drawing upon experience with the similar HCFC compounds they replace, interference with scientific analyses is not anticipated with either HFC or HFE densifiers.

Introduction

It is well known that deep drilling in glacial ice requires the use of a borehole fluid. Borehole fluid provides hydrostatic compensation, necessary to prevent closure of the borehole due to "lithostatic" pressure of the surrounding ice.

A number of different fluids have been applied, with mixed success, in previous deep glacial drilling operations. Failures have been many, and can be attributed to various causes. Some of these causes are examined below.

Fluid Properties

The ideal drilling fluid would simultaneous meet several different and somewhat conflicting criteria:

Density: The fluid would have {density *vs.* temperature}, and {compressibility *vs.* pressure} characteristics that would allow a column of this liquid to exactly mimic the lithostatic stress within the ice as it varies with depth.

Volatility: The fluid would be highly volatile, so that it would evaporate cleanly, completely and rapidly from the ice-cores. It should not interfere with any of the subsequent analytical procedures, or with any that might be conceived and developed during the archival life of the core.

Flammability: The fluid would be non-flammable, non-explosive, etc.

Freezing Point: The fluid must remain liquid and of low viscosity throughout the vertical extent of the column

Reactivity: The drill fluid would not react in any way with the ice core, nor with the walls of the borehole, nor with the chips produced by mechanical drilling operations; it should not be in itself corrosive or form corrosive decomposition products. It should be non-conductive to minimize problems with electrical apparatus in the borehole.

Toxicity: The drilling fluid would be completely non-toxic to humans, and 100% biodegradable with very short half-life and no biological concentration/amplification effects, and have no other environmental effects (such as, but not limited to, Ozone Depletion Potential, or "ODP" and Global Warming Potential, "GWP")

Viscosity: As the drill itself must move up and down in piston-like fashion through the column of drilling fluid, it is imperative that the fluid has the lowest practical viscosity so as to minimize trip time and energy expenditure.

Cost: The fluid should be intrinsically low in cost, and readily available from markets nearest to the site of drilling operations to minimize transportation costs.

Simultaneous satisfaction of all these criteria is impossible, and so intelligent compromises are required. For example, these fluids contain without exception at least one organic compound and so the desirability of high volatility frequently conflicts with the desirability of low flammability.

Major classes of fluids are examined in the next section.

Hydrophilic vs. Hydrophobic fluids

Fluids for ice drilling can be broadly classified as hydrophilic ("water-loving") or hydrophobic ("water-fearing"). Anti-freeze solutions consisting of ethanol + water, ethylene glycol + water, etc., are all intrinsically hydrophilic.

Hydrophilic solutions can be prepared so as to have the appropriate pressure-compensating density and have intrinsically low flammability, generally low toxicity, relatively low cost, low environmental hazard potential and other desirable characteristics. However, these desirable characteristics are entirely negated by the fact that these solutions are reactive in the presence of ice; they continuously dissolve the borehole walls, the core, and chips until slush forms. During this process, the density of the hydrophilic solution undergoes continuous change resulting in convection. If this process is allowed to continue, the borehole is eventually rendered unusable. Given an initially uniform solution concentration, slush will most likely form first in (or near) the coldest part of the borehole and may result in closing the borehole above the drilling equipment, resulting in the loss of the equipment.

For the purposes of deep electromechanical drilling in very cold (less than ~ -30º C) ice, especially given that the borehole may be required to stay accessible for many years, experience has demonstrated that hydrophilic fluids are not suitable.

Hydrophobic, or *effectively hydrophobic*, fluids include those composed largely of organic solvents. Many of these solvents are also used as fuels. Examples of these are the turbine fuels (JP-4, -8, etc.), the de-aromatized industrial solvents (e.g., Exxon™ Exxsol™ D-60, - 40, -30). These solvents and fuels are all essentially comparable to kerosene and differ only in the details.

To produce a suitable drilling fluid these low-density solvents (or fuels) are blended with partially-to-fully-miscible, high-density organic compounds to increase the fluid's density to roughly 0.93 g/cc. The "densifiers" are chiefly halogenated hydrocarbons, chlorofluorocarbons, hydrochlorofluorcarbons, etc. such as trichlorethylene, perchlorethylene, HCFC-141b, HFC-123, CFC-11, etc.

A few organic compounds have suitable density when used alone. An example is n-butyl acetate ("NBA").

These "hydrophobic" compounds (or mixtures of compounds) may dissolve a small amount of water from the borehole environment but this amount is small and strictly saturation-limited. The fluid's interaction with water in the solid-state may have other, non-intuitive effects, referred to later in this document.

A number of other hydrophobic compounds (or mixtures) have been proposed as drilling fluids in deep ice and they have been rejected on various grounds. Talalay and Gundestrup (1999) suggested silicone (dimethylpolysiloxane) fluids, but they are very expensive, and may not be readily available in quantities approaching the required 50,000 liters.

Also, silicone fluids may be neither as environmentally nor toxicologically innocuous as Talalay and Gundestrup (1999, 2002a) suggest. For example Nashua Corporation[1] indicates that dimethylpolysiloxane:

- Causes eye irritation upon contact;
- Can cause respiratory irritation and sensititization due to formaldehyde that is released upon thermal decomposition (T > 150º C);
- "Dimethylpolysiloxane is a questionable carcinogen with experimental neoplastigenic data. This compound is also considered tumorigenic by RTECS criteria[2]"
- Repeated skin contact may lead to development of dermatitis (dry red, cracked skin). *This compound is a suspect carcinogen and reproductive toxin* [emphasis added]
- When discharged in large quantities, aquatic life may be harmed. The L_C50 for bluegill and rainbow trout species is 10g/liter.

There have also been media reports of sensitization and reaction of the immune system due to exposure to supposedly "inert" silicone-bearing surgical implants.

This author's experience in the field of mass spectrometry shows that silicone compounds can polymerize to form dielectric films when bombarded by electron beams or charged particles, resulting in beam-deflecting charge accumulations within the vacuum chamber. It should be noted that much of the analytical work with ice cores is in the field of mass spectrometry.

Because of the low volatility and limited solubility of silicone oils, it is difficult to thoroughly clean silicone-oil contaminated surfaces; it is likely that silicone oils would be a nightmare for those processing and analyzing ice cored using silicone-based drilling fluids. Removal of silicone fluids from core surfaces would require further processing (washing) in other solvents; these solvents would then need to be stripped of the dissolved silicone compounds by distillation. In the drilling area, slippery and persistent silicone-fluid films would eventually contaminate all working surfaces, tools, clothing,

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[1] MSDS #4103; Fuser Oil and Fuser Oil Lubricant; Nashua Corp., Merrimack, NH., 03054)
[2] see also: NIOSH-RTECS # TQ2690000

etc. Clothing would require "dry-cleaning" on-site and (again…) the distillation of cleaning solvents.

Of the silicone compounds, only the group known as volatile methyl siloxanes (VMS) will evaporate cleanly. An example of this group is Dow Corning™ 200(R) fluid, which is predominantly hexamethyldisiloxane. It is unsuitable as a drilling fluid because it is too low in density to be used as a densifier (specific gravity ~ 0.76), and is quite flammable (NFPA Flammability rating = 3; flash point only –3.3º C; flammability limits in air 1.5% to 14.7%) and produces formaldehyde gas and silicon dioxide dust upon combustion.

Brominated compounds such as tetrabromoethane (TBE) and polybrominated biphenyl ether (PBBE) have been suggested but not used for drilling of ice, as these are both extremely toxic and resistant to biological degradation, and have technical limitations as well.

Single Component Hydrophobic Organic Fluids: n-Butyl Acetate

To date, only one single-component fluid has been used to any extent. This fluid is n-butyl acetate, also known simply as "butyl acetate." Synonyms include "butyl ethanoate," and "acetic acid butyl ester." Hereafter, it is referred to as "NBA."

NBA is isomeric with isobutyl acetate, sec-butyl acetate, and tert-butyl acetate, sharing the same formula ($C_6H_{12}O_2$) and molecular weight (116.16 g/mol). However, the other physical properties vary from one isomer to another. For NBA itself, the following apply:
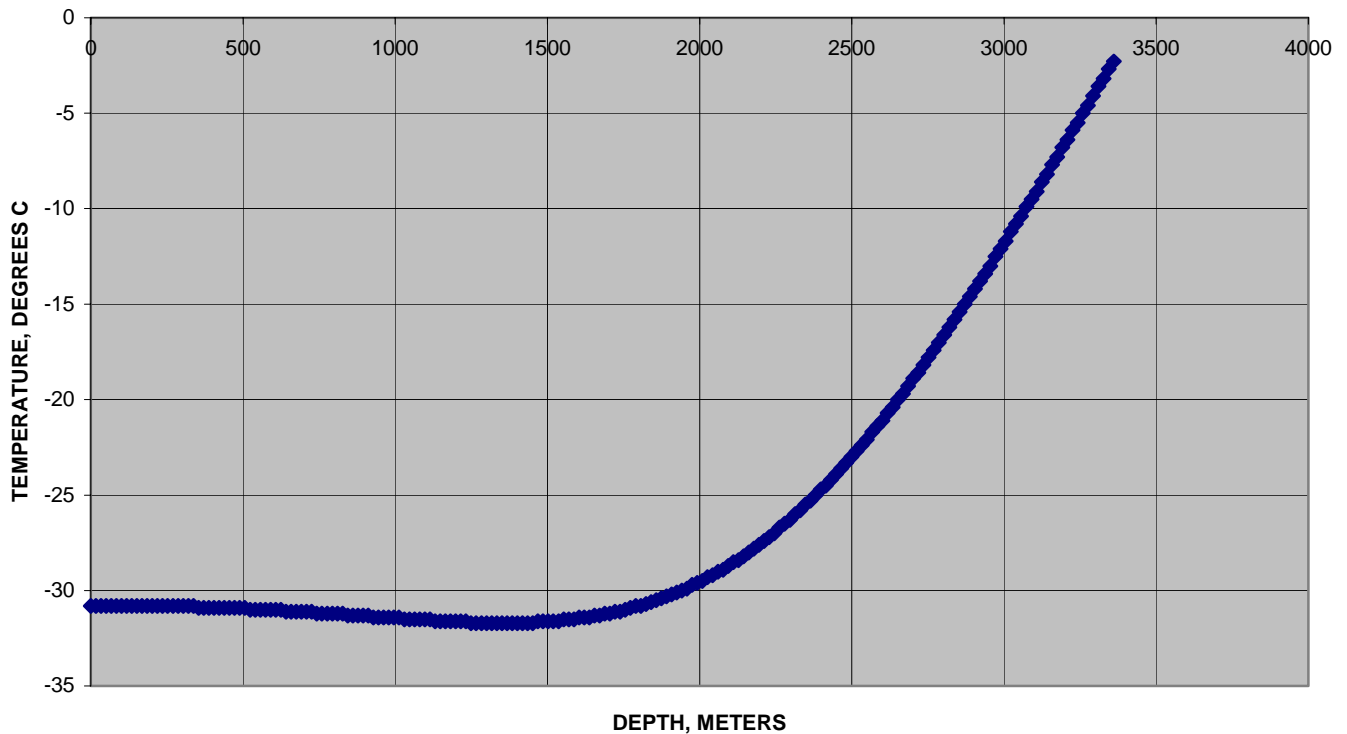
- Boiling Point = 127º C
- Melting point = –77º C
- Specific Gravity (@ 20º C) = 0.9
- Vapor Pressure @ 20º C = 1.07 kPa
- Specific Vapor Density (air = 1.00) = 4.0
- Closed Cup Flash Point = 24º C
- Explosive Limits (volume % in air) = 1.2 to 7.5
- Odor threshold = 10 ppm
- NBA is miscible with alcohol, ether, ketones, esters, most hydrocarbons and other organic solvents[3]

NBA was the drilling fluid of choice for the GISP2 project headed by PICO, University of Alaska and was also used by the JARE Dome Fuji project, Antarctica.

Strictly in terms of borehole pressure compensation, for cold ice conditions such as exist in Greenland and in Antarctica, NBA is a nearly ideal drilling fluid. As demonstrated by Talalay and Gundestrup (2002a), the {pressure *vs*. depth} characteristic curve for NBA, once corrected for temperature and compressibility effects, matches the projected ice

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[3] *(Data from Report no. 2001/030SH; Dutch Expert Committee on Occupational Standards [DECOS], The Hague, 2001)*

FIGURE 1: WAIS THEORETICAL TEMPERATURE PROFILE

pressure very closely and resulting in stable borehole geometry (see WAIS temperature profile, Figure 1[4]). NBA has not been reported to react in any way with chips to form chip cakes, floating or sinking ice-chip rafts, etc., and the saturation concentration of water in NBA is low (1.6 g/l, or about 1600 ppm, at 25º C).

Talalay and Gundestrup (2002b) noted that the JARE project at Dome Fuji, utilizing NBA, resulted in a stuck drill. Drilling continued during the over-wintering season even though the crew ran short of NBA, resulting in the unacceptable lowering of the fluid level in the borehole to 720 meters below the surface. It was known that somewhere in the range of 2000 to 2500 meters the ice begins to experience rapid increase in temperature and plasticity, but drilling was continued with concurrent reaming, and reached a depth of 2503 meters. Reaming was insufficient to overcome the increasing closure rates, and the drill was stuck at this depth. This failure was the result a lost gamble, unrelated to the choice of NBA as a drilling fluid. However, this initially encouraging picture must be tempered with observed facts about NBA: a very aggressive solvent nature, its toxicity, and flammability.

The use of NBA presents a number of engineering challenges due to its aggressive and somewhat unique solvent characteristics. It is capable of dissolving oils, fats, waxes, camphor, rubber, synthetic resins / polymers of many kinds, and many other substances. NBA is widely used as a solvent or carrier in the leather, paper, coatings, chemical processing and extraction industries, and for dissolution of nitrocellulose.

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[4] Data supplied by K. Taylor (*pers. comm.*, 2003)

NBA will strip paint from equipment that comes into contact with it. The effect of NBA upon the bond strength of glue in various types of plywood, as used extensively in field-camp construction, is not known.

NBA decomposes in the presence of water to form acetic acid that is in turn corrosive to metal, electrical and electronic components, etc. This decomposition is likely to be inhibited by low temperatures but is still a cause for concern.

NBA is flammable, at least at normal room temperatures, but otherwise chemically stable except in the presence of acids, bases, oxidizing materials etc. It will not [explosively] polymerize.

Due to the low temperature at the drilling site, the flammability hazard is decreased. The vapor pressure at –20ºC is only 0.07 kPa whereas at +20ºC it is about 1.0 kPa). Vapor loading of the ice-drilling work area decreases by a factor of nearly 15: 1 compared to what might exist in a workplace at room-temperature conditions and similar wetted area. According to Gosink *et al.,* (1994), the vapor pressure of NBA is such that the lower flame limit concentration (stated therein as 1.4%) of NBA in air would not be reached except in an enclosed container [therefore reaching equilibrium conditions] at [or in excess of] 24° C [5]. Thus, the fire hazard was considered to be minimal (Gosink *et al.,* 1994[6]).

Although the ambient temperature in the drilling area will be less than the flash point for NBA, danger would be associated with locally higher temperatures such as near space-heaters, warm electrical apparatus, enclosed areas (including the drill-operator's kiosk) where NBA-contaminated clothing is drying, etc. This latter problem is compounded by static discharge in the warm-air, low-humidity environment.

The toxicology literature for NBA is extensive. NBA is listed as a Right to Know (RTK) substance (#1329) by the State of New Jersey and is cited because of its fire and explosion hazard, reproductive risk, and a number of exposure risks including eye, skin, and respiratory tract irritation. Anecdotal evidence from drilling operations includes reports of headaches and nausea stemming from the narcotic effect of inhaled NBA fumes. During the GISP2 project (Gosink *et al.,* 1991), forced ventilation reportedly lowered the fume concentration to less than 100 ppm; the concentration reached 40 ppm near the drill collar and elsewhere was reported at about 10 ppm. In spite of such good ventilation, organic-vapor-cartridge respirators were also supplied. That some of the personnel experienced health-related problems following exposure despite the conditions reported by Gosink et al. (1991) suggests hypersensitivity to NBA, individual exposure to higher concentration levels, and/or exposure for longer periods of time. The short and long term influence of alcoholic beverages may also play a role (see below). According

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[5] 10mm Hg vapor pressure / 760 mm Hg air pressure = 1.3% concentration v/v assuming Ideal Gas behavior (vapor pressure data quoted in Gosink et al., 1994)

[6] Gosink's (*et al.,* 1994) exposition is an awkward re-statement of the definition of the closed-cup flash-point test.

to at least one report from NGRIP (L. Augustin, *pers. comm*., 2003), a single barrel of NBA was added to the borehole fluid more than two years ago and became highly diluted, but headaches still result from breathing the fumes.

Acute toxicology for humans includes the aforementioned narcotic effects as well as irritation to eyes, respiratory tract, and skin. OSHA found that workers

"… are at a significant risk of experiencing the severe, eye, skin and respiratory irritation, in addition to narcotic effects, … associated with short-term exposures to this substance above the 8-hour [150-ppm, TWA] limit. [OSHA] considers the irritant and narcotic effects resulting from exposure to n-butyl acetate to be material impairments of health and functional capacity. OSHA concludes that a STEL [short-term-exposure-limit] is necessary to reduce this risk, and [OSHA] is therefore revising its limit for n-butyl acetate to 150 ppm as an 8-hour TWA and 200 ppm as a 15-minute STEL" (www.cdc.gov/niosh/pel188/123-86.html).

According to the report issued at The Hague by the Dutch Expert Committee on Occupational Standards (DECOS, 2001), NBA and its isomers would be "readily absorbed by the respiratory tract, the skin, and the gastro-intestinal tract." NBA has an NIOSH- IDLH rating[7] of only 1700 ppm.

In experimental studies of the kinetics of the isomers, the DECOS report noted the following partition coefficients {tissue *vs.* blood} were found for the rat:

- Fat 17
- Liver 3.14
- Kidney 2.72
- Brain 1.85
- Muscle 1.76

The rat {blood *vs.* air} partition coefficient was found to be 1160; somewhat higher when compared to the human {blood *vs.* air} ratio of 670.

NBA is, however, rapidly metabolized. DECOS (2001) reports that, i*n vitro*, the half-life of NBA in human blood is only about 4 minutes, while *in vivo* studies in the rat (at dosage rates of about 30 mg/kg, i.e., 30 ppm w/w) indicate that hydrolysis within the blood and brain were essentially complete within 3 minutes.

DECOS (2001) also reported that *ethanol inhibits or retards metabolism* of butyl-acetate isomers, likely by competing for the same metabolic substrates [assumed: in the liver, and elsewhere]. Groth and Freundt (1991) observed that simultaneous inhalation of NBA by rats with, and without, administration of ethanol led to NBA concentrations in blood being *doubled* by co-administration of alcohol.

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[7] www.cdc.gov/niosh/idlh/123864.html

Based on this observation alone it would seem prudent to limit the consumption of alcoholic beverages among those exposed to NBA; this might be only possible through the enforcement of an outright ban on alcoholic drinks at the field location.

The intense nature of the ice-coring operations engendered by the limits of a short season and remote conditions mean that drilling personnel are often on the solvent-contaminated site of operations for up to 14 hours each day, allowing only time for eating and sleeping; even sleeping-quarters can be a source of exposure to fumes if contaminated clothing is allowed to be brought there. Either strict workplace hygiene must be observed or the exposure limit during the 8-hour working day must be significantly adjusted downward in compensation, if health is not to be affected by excessive loading.

There is evidence of reproductive harm such as reduced birth weight (DECOS, 2001), and fetotoxicity (such as stunted fetus and developmental abnormalities)[8], at least for the offspring of sub-chronically-exposed female laboratory animals; the DECOS report indicates that the limited extent of the study itself made the results "inconclusive."

Chronic exposure toxicity, reproductive harm (teratogenicity), and carcinogenicity studies are lacking, but *in vitro* mutagenicity of bacteria and yeast, and genotoxicity tests on Chinese-hamster fibroblasts were both negative (DECOS, 2001). These data suggest that, *at the very least*, female employees of child-bearing age should be informed of probable short-term, and unknown long-term reproductive risks associated with exposure to NBA.

Based on the available data, DECOS (2001) recommended a "health-based occupational exposure limit" for n-butyl acetate of 150 mg/m^3, about **30 ppm.** This is only *one fifth* of the NIOSH / OSHA 8-hour TWA and only three times the threshold of detection by odor.

It would seem prudent that the use of NBA, with its long daily exposure period and the strenuous remote conditions which accompany polar drilling operations, would be attended by careful monitoring of the worksite by a qualified industrial hygienist / technician, and that equipment for determining NBA concentrations in air be available on-site. It would be scandalous if workers were exposed for an entire field season to excessive vapor concentrations, a condition revealed too late by subsequent off-site processing of samples. As noted above, previous PICO operations supplied workers with respirators fitted with organic-vapor cartridges and these need regular cleaning, disinfections, maintenance, fitting, and testing; this is also a task for a qualified professional or technician.

The effect of decreased atmospheric pressure, due to high altitude operation on polar plateaus, on NBA toxicity is not known. However, use of filtration-type respirators will contribute to the respiratory stress already being experienced due to high altitude. Due to the stress they place on the respiratory system, filtration-type respirators are generally regarded as a second line of defense, with the primary defense being workplace environmental control.

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[8] NIOSH-RTECS #AF 7350000; 2002

From an environmental standpoint, NBA is harmful to aquatic organisms[9] and is described as "moderately toxic to aquatic life."

The highly aggressive, broad-spectrum solvent nature of NBA makes it a challenge from an engineering standpoint. NBA softens, dissolves, shrinks, swells, or causes crazing (cracks) in many polymers, synthetic rubber or "elastomer" components. These include the seals on rotating or reciprocating shafts and pressure chambers, electrical insulation, plastics and electrical insulating varnish; it strips paints and other protective coatings from surfaces, and so forth. It was implicated in the premature failure of the Kevlar™-based electromechanical cable of the GISP2 project.

For NBA, it is not prudent to rely on tabulated chemical compatibility data; for example, some manufacturers' varieties of high-density polyethylene (HDPE) are compatible whereas others are not[10]. Therefore individual testing of components is required in advance of application and tested batches of components should be stockpiled to avoid substitution with components of unknown pedigree and suitability. Such precautions are common in the aerospace industry, where even mundane components have an extensive "paper-trail" attached to them.

Use of NBA as a drilling fluid can be expected to compromise reliability and increase costs of design, testing, and production when compared with less-aggressive and less toxic fluids. Sufficient spares would have to be available on-site for all polymer / elastomer parts that come into contact with NBA, including suspension cable (polymer electrical insulation) and much of the drill sonde. Breaching of fluid seals into the pressure-tight electronic instrumentation section would be catastrophic, as NBA would quickly attack sensitive components and insulation on printed circuit boards. A damage-monitoring program would have to be instituted.

In short, the engineering and operations team would be required to "expect the unexpected."

Two-Component Organic, Hydrophobic Drilling Fluids

All two-component drilling fluid systems employed to date consist of a kerosene-like petroleum base that, by itself, doesn't have sufficient density to accomplish full hydrostatic compensation. The density is boosted by blending in another, higher density compound. Without exception, those "densifier" compounds are a type of halogenated hydrocarbon *(sensu lato).*

Petroleum-plus-densifier drilling fluid was first applied to the boreholes at Camp Century and Byrd Station, accomplished by CRREL during the period 1966-1968. These used Arctic Diesel fuel and Trichlorethylene in the upper part of the fluid column, with a lesser

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[9] Matheson Tri-Gas, Parsipanny NJ USA; www.inchem.org/documents/icsc/eics0399.htm

[10] *Chemical Resistance of Plastics and Elastomers;* Third Edition; Plastics Design Library, 2001. Available as a *Knovel's* on-line reference.

amount of (immiscible) aqueous ethylene glycol solution at the bottom of the borehole. It seems likely that glycol-water slush contributed to the sticking of the drill during the resumption of drilling in the second season at Byrd Station (Talalay and Gundestrup, 1999, 2002).

Two-component systems have the advantage of allowing the density of the fluid to be tailored to any value in the range between that of the pure petroleum base stock, and that of the "densifier." Due to the variation in accumulation rate, mean annual surface temperature, and geothermal heat, both pressure and temperature are a variable function of depth in the world's glaciers; the choice of the mean density of the borehole fluid is therefore important.

The minimal requirement is attainment of equilibrium compensation conditions before relatively warm ice is penetrated, and maintained thereafter, in order to prevent rapid borehole closure (Talalay and Gundestrup, 1999). At depths less than the chosen equilibrium-compensation point, cold and relatively less-plastic ice predominates, and under -compensation is less precarious.

Although not generally practiced to date, the limited degree to which the column of fluid is mixed by the passage of the drill allows tailoring of the density (pressure) profile by delivering densifier or pure petroleum solvent to the various levels employing a "tank-car" in place of the drill.

The Petroleum Base-Fluid

All of the two-component systems employed to-date use a petroleum base (about 75% by volume) comparable to kerosene. These have included "Arctic Diesel" fuel, jet fuel A-1, turbine fuels of the class JP-4, JP-8 etc., Exxsol™ D-30, D-40, D-60 etc. Functionally these are all very similar and differ in minor ways such as the content of aromatics, waxes, sulfur, and other impurities.

These products are similar in price, readily available in bulk (often with minimal notice), are widely distributed worldwide, and are much less expensive than the densifier component they are mixed with. The Exxsol™ D- series of solvents are kerosene-like solvents that have been processed ("hydro-treated") to remove aromatic hydrocarbons. D-40 typically contains only about 0.01% aromatics whereas kerosene and related fuels have aromatic contents of about 10 to 20%. Removal of aromatic hydrocarbons (such as benzene) sharply reduces the solvent's odor as well as the health hazards associated with aromatic exposure. These D-series solvents have been extensively employed in the European EPICA program including the NGRIP project that successfully reached bedrock 17 July 2003, at a depth of 3085 meters.

Higher-purity paraffinic solvents of this class exist (the Norpar™ and the Isopar™ range of products of Exxon™, for example) and may be desirable from the standpoint of sample cleanliness and worker health for a minimal increase in cost. Isopar™ is so pure as to be applicable to the manufacture of cosmetics and the application of waxes and other

coatings to food products. They are only about 10 cents per liter more expensive than the equivalent Exxsol™ D-range.

Because such a large quantity of petroleum base fluid is required, and de-aromatized solvents are so readily available, it doesn't make sense to rely on JP-8 or any other fuel product containing harmful aromatic compounds.

The manufacturer's recommended TWA for Exxsol™ D-40 is 200 ppm (~ 1200 mg/m3). NIOSH stipulates only 14 ppm (~100 mg/m^3) for Kerosene, reflecting the greater hazard posed by the aromatic content of Kerosene and related fuels (JP-8 etc.).

De-aromatized or pure paraffinic petroleum solvent meets the overall desirable characteristics of good volatility and clean evaporation, relatively low flammability (especially at low temperatures), and low toxicity. They are also useful as incidental cleaning solvents for machinery and (in appropriate appliances) as a fuel for space heating, etc. They have minimal environment-hazard potential.

Densifiers

As previously noted, several halogenated hydrocarbons *(sensu lato)* have been used as densifiers. They range in specific density from about 1.24 (for HCFC-141b) to 1.63 (perchlorethylene).

As previously noted, Trichlorethylene was used by CRREL at Camp Century and Byrd Station. It is a colorless, non-flammable, non-corrosive liquid with a sweet odor. It has been implicated as a possible carcinogen by OSHA and other agencies and has serious central nervous system effects at exposure levels in excess of 50 ppm. Therefore, current OSHA exposure limits are a 50 ppm TWA PEL and a 200 ppm STEL. The New Jersey Department of Health and Senior Services considers trichlorethylene to be a Right To Know (RTK) substance (#1890) and specifically identifies it as a mutagen.

In 1980-81, the University of Copenhagen chose perchlorethylene (a.k.a., tetrachloroethylene) as the densifier for the DYE-3 drill program. Perchlorethylene has, like trichlorethylene, been implicated as a carcinogen (especially of the liver). The OSHA 8-hour TWA exposure limits for perchlorethylene is 100 ppm with 5-minute exposure limit in any three-hour period of 200 ppm. The New Jersey Department of Health and Senior Services considers it to be a Right To Know (RTK) substance (#1810) and identifies it as an occupational carcinogen.

The chlorofluorocarbon compound CFC-11 (a.k.a., trichlorofluoromethane; Freon™ 11 or Refrigerant 11, etc.) is a clear, colorless liquid with faint ethereal odor. It was employed by the USSR's program at Vostok Station during 1986-1989. The Montreal Protocol identified CFC-11 as a "Class 1 Ozone Depleting Substance" due to its high Ozone Depletion Potential (ODP) and it is no longer available due to compliance with the Protocol.

CFC-113 (Freon™ 113) was used at GRIP (University of Copenhagen) during 1990-1992 but it, too, has been banned under the "Montreal Protocol."

Most recently, the chlorofluorocarbon HCFC-141b has been employed at North GRIP (NGRIP; University of Copenhagen), Dome Concordia (West Antarctica; EPICA program), Dronning Maud Land (East Antarctica; EPICA program), and in the completion of the Russian Vostok - station borehole. The latter holds the current world-record depth at 3623 meters.

The Montreal Protocol placed HCFC-141b on its Class II substance list. Originally, Class II compounds were slated for restrictions starting in year 2015 and outright prohibition by 2030. The US-EPA accelerated this process within the USA and HCFC-141b is now under a production-and-import ban. The accelerated phase-out was largely a response to the commercial availability of suitable, low ODP, replacements. What follows, then, is largely of historical interest and for comparison purposes with proposed substitutes.

NIOSH and OSHA set the TWA for HCFC-141b at 1000 ppm. In large concentrations it can act as an irritant to the respiratory system or a simple asphyxiant. HCFC's such as –141b have the capacity to sensitize the heart to adrenaline (or its synthetic equivalent, epinephrine), resulting in cardiac arrhythmia and possible cardiac arrest. It is interpreted here, that the latter is a transient (acute-exposure) effect but this is not perfectly clear from any of the documentation examined. It would be a matter of grave concern if the sensitization were cumulative and /or permanent.

HCFC-141b is not flammable (it has no discernable flash point) but may decompose on contact with flames or very hot surfaces (example: electric-resistance heating elements as used in space heating) to form toxic and corrosive products. In this way, it is reminiscent of carbon tetrachloride (a.k.a. Freon™ 10, or tetrachloromethane) that forms deadly phosgene gas when heated. HCFC-141b is relatively non-reactive with metals but causes swelling and other deterioration of many elastomeric compounds.

HCFC-141b is blended batch-wise with the petroleum solvent base-stock to the correct, temperature-corrected density before being added to the borehole. Drilling fluid additions are made whenever the fluid level in the borehole drops below a predetermined "minimal" level due to continued boring and carry-out.

HCFC-141b has been noted to bond, to a limited extent, to ice chips within the borehole and thereby increases their density (Talalay and Gundestrup, 1999; Gundestrup et al., 2002). Over a long period of time such chips may sink to the bottom of the borehole to form slush. Under conditions of normal drilling this does not appear to be a problem but may contribute to sticking of the drill when the driller is unaware of the possibility of a slushy bottom following a long period (such as the over-winter down time) of inactivity. Good drilling practice strives for complete chip recovery, and strict filtering and other precautions at the end and beginning of drilling seasons can contribute to trouble-free operation.

Towards a Densifier to Replace HCFC-141b

Most of the world's consumption of HCFC-141b was as a non-flammable safety solvent in the electrical and precision instruments industries, and as a "blowing agent" for rigid foam insulations. Compliance with the Montreal Protocol, variously updated over time, has severely restricted the application of chlorofluorocarbons (mostly Class I ozone-depleting substances) and hydrochlorofluorocarbons (mostly Class II ozone depleting substances). The solvent production and end-use industries have been hard at work to develop alternatives. Many of these have received approval from the US-EPA under the SNAP program.

Several compounds have been competitively marketed to various industry sectors. None of them duplicate, exactly, the characteristics of HCFC-141b and so the choice is dependent upon end-use. The HCFC-141b alternative products include:

- Volatile methyl siloxanes (VMS: mentioned previously)
- N-propyl bromide
- Hydrochlorofluorocarbons such as Asahi Glass Company™ HCFC-225 ca/cb
- Cyclopentane and isopentane blends such as Exxsol 2000™ Blowing Agent;
- Perfluorocarbons (PFC's) such as the Fluorinert™ liquids from 3M™ Corporation;
- Hydrofluoroethers (HFE's);
- Segregated hydrofluoroethers (Segregated HFE's) such as Novec™ fluids from 3M™ Corporation;
- Hydrofluorocarbons (HFC's) such as Vertrel™ from DuPont™ (HFC-43-10 mme) as well as HFC-365mfc

In addition, many companies are marketing proprietary solvent blends tailored to specific needs. Many of these solvent blends are azeotropes targeted for vapor-bath degreasing applications; none are directly suitable for use as a borehole fluid and so this discussion concentrates on the pure solvent end-members.

N-Propyl Bromide

N- prophyl bromide has been suggested as a substitute solvent for HCFC-141b in the electronics (circuit board cleaning etc.) industry. However, a review of the toxicology literature indicates that this compound is not really suitable for use in situations other than closed systems. Atofina™ Corporation refuses to market this product for anything other than closed-system applications[11].

The toxicological data, while incomplete, are sufficient for our purposes: n-propyl bromide is toxin that targets the liver, kidney and other organs, as well as the nervous system; it causes severe respiratory, eye and skin irritation and is teratogenic (causes

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[11] ECSA newsletter, November 2002, No. 22, page 2

reproductive harm). The US EPA plans to regulate NPB, allowing its use "as a substitute for ODS with certain [attached] conditions because of its toxicity and potential health effects on people who are exposed to it."[12] The States of Massachusetts, New Jersey, and Pennsylvania all consider NPB to be a RTK substance.

We can effectively discount any further consideration of this compound as a substitute in our (rather arcane) application.

Hydrochlorofluorocarbon Substitutes:

There is only one readily available HCFC substitute for HCFC-141b, and that is HCFC-225 ca/cb[13] produced and marketed by Asahi Glass Company ™ of Japan.

As HCFC-225 ca/cb is bound under the Montreal Protocol (it is a Class II Ozone Depleting Substance) to be removed from the marketplace starting in 2015 and to be completely removed no later than 2030, it does not make sense to make a commitment to HCFC-225ca/cb as our densifier product. Like HCFC-141b, it could become subject to an accelerated phase-out by the US-EPA. Presently it is also one of the most expensive alternative products.

Cyclopentane / Isopentane Blends

Besides being highly flammable, these substitutes being marketed to the foam insulation industry as blowing agents, have too low a density (~ 0.75 g/cc) to be used alone or as a densifier.

Perfluorocarbons:

These are extremely stable compounds composed of very long chains of carbon atoms completely surrounded on all potential atomic bonding sites by fluorine atoms. The high strength of the carbon-fluorine bond accounts for their extreme stability and extremely low toxicity. They are very low in viscosity, have very low freezing points and have zero ozone depletion potential. They have high density, in the range of 1.5 to 1.7 g/cc, and this also makes them very enticing. PFC's have zero ODP but their stability means that they do not readily break down in the environment and this contributes to their very high GWP (typically 5000 to 10,000).

PFC's (such as 3M™ Fluorinert™ FC-87™) are immiscible except in other fluorinated compounds, and this makes it impossible to blend a drilling fluid of suitable density using an inexpensive hydrocarbon base such as Exxsol™ D-40 or D-30. So, we can effectively discount the application of PFC's in the formulation of a drilling fluid.

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[12] US-EPA Document EPA-430-F-01-039 / June 2003
[13] The "ca/cb" suffix refers to the two isomers of the compound found in the commercial formulation in the ratio of about 55% : 45% respectively

Hydrofluoroethers and Segregated Hydrofluoroethers:

Hydrofluoroethers are chain-structures of carbon dominantly bonded to fluorine and in this way they are similar to the unadulterated {carbon + fluorine} PFC's, but HFE's also containing oxygen, and hydrogen. An oxygen atom forms the link between a long chain of perfluorinated carbons (think of this as a PFC molecule, or radical), and one or more carbon atoms that are bonded only to hydrogen. Thus the molecule is segregated into two distinct portions joined by the oxygen atom.

Ordinary hydrofluoroethers may have zero ODP, but they exhibit extremely high (low hundreds to about 15,000) GWP. They do not appear to be readily available in the marketplace. However, segregated HFE's with GWP's typically about 50- 400 are readily available. These include compounds such as 3M™ Novec™ HFE-7100 and HFE-7200 fluids. Under SNAP, HFE-7100 and HFE-7200 are approved for use "without restriction[14]."

The oxygen ("ether") atomic bond in these "segregated" hydrofluoroethers acts as a weak link and, once released into the atmosphere, the molecule begins to un-ravel at this oxygen bond. Because of this unraveling, the atmospheric lifetime of the segregated HFE compound is very sharply reduced (1-5 years) compared to its un-segregated HFE relatives (2000-3500 years), sharply limiting its GWP.

Segregated HFE's such as HFE-7100 and HFE 7200 have density of about 1.4 to 1.5 g/cc, low viscosity, very low toxicity, no flash point, and extremely low toxicity. They have a vapor pressure significantly higher than Exxsol™ D-40 but lower than HCFC-141b; drilling fluids can be prepared using less of these compounds as densifier and with less loss due to evaporation during handling of chips and core. Everything else being held constant, vapor loading of the work area would decrease, requiring less ventilation power. Both the hydrocarbon solvent and the densifier evaporate cleanly, without residue.

Hydrofluorocarbon (HFC) Substitutes

Two HFC products are being marketed to replace HCFC-141b in some applications. These are HFC-365mfc, about to be released to market by Atofina™ Corporation, and Vertrel XF™ from DuPont™ Corporation (their proprietary name for HFC-43-10mme).

HFC-365mfc is a chlorine-free replacement for HCFC-141b about to be marketed (summer 2003) by Atofina™. In this pre-release stage, the product data is, for now, sparse.

Although being marketed to the former users of HCFC-141b, HFC-365mfc is flammable, highly volatile, and has a low flash point. Table 1 (data compiled from various published sources) allows at-a-glance comparison of these important parameters:

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[14] 3M Corporation Document 4398 (HB) / 98-0212-2649-7/ January 2003

	HFC-365mfc	AVGAS	VM&P Naphtha	NBA	Ethanol
Vapor Press. @ 20C (mm Hg)	417	200	20	10	44
Vap. Density (air = 1.0)	5.1	3	( )	4	( )
Boiling Point, C.	40	>20	95-160	126	78
Flash Point, C.	minus 24	< minus 40	minus 7, to 13	22	22
L. Expl. Limit, % (@20C)	3.5	1.4	1.2	1.7	3.3
U. Expl. Limit, % (@20C)	13	7.6	6	7.6	19
DOT Hazard Class	3	3	1B	1B	1B

Table 1

HFC-365mfc is *not* a one-for-one replacement for HCFC-141b in industry where the latter is used as a non-flammable "safety-solvent". In fact, HFC-365mfc is comparable in flammability to Aviation Gasoline (AVGAS) and has a lower flash point than even Varnish Makers' and Painters Naphtha (VM&P Naphtha).

Available data, including the MSDS, emphasizes that HFC-365mfc is flammable and must be handled with great care to prevent explosions, and would (unlike simple flammable hydrocarbons) produce highly toxic decomposition products such as carbonyl halides[15] and hydrofluoric acid should a fire erupt.

The low flash point, high vapor pressure and wide explosive limits of HFC-365mfc are particularly worrisome for drilling under polar conditions, considering that:

- Ventilation systems moving air at high speed will produce static discharges
- Fan-belts will produce static discharges
- Friction of synthetic clothing materials will produce static discharges
- Tools may produce sparking when in use
- Electrical equipment will produce sparking at commutators and faults, *etc.*
- ***Due to the dielectric nature of the glacial ice and snow, there is no way to effectively procure a grounding point at the drill site (until drilling is completed to bedrock, of course)***

Another unexpected issue with HFC-365mfc recently revealed in the data from Atofina™ Corporation is that the freezing point for this compound is a mere –35º Celsius. This would mean that the compound would have to be guarded against freezing for much of the transport and storage cycle, unless it were to be diluted prior to transport to Polar locations with a quantity of petroleum solvent. Petroleum solvent alone has a very much lower freezing point (roughly –60º C).

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[15] Phosgene (gas) is an example of such a compound

It should be obvious that HFC-365mfc does not meet the criteria for a densifier that would be safe and convenient to handle.

On the other hand, HFC-43-10mme[16] (DuPont™ Vertrel XF™) satisfies the issue of fire safety by being, like HCFC-141b, without a flash point or explosive limits. Like all HFC's and HCFC's, it can decompose thermally in a fire to produce toxic substances but this is made highly unlikely by the lack of flash point. The flash point of the co-solvent Exxsol™ D-40 is + 42º C, very much higher than ambient conditions encountered in ice drilling. The very low toxicity, high liquid density (1.58 g/cc), miscibility with hydrocarbon fluids, vapor pressure, ODP, and GWP of this compound are all very promising; it merits closer examination in the laboratory to simulate drill conditions such as chip agglomeration.

Discussion: HCFC-141b "Densifier" Substitutes

HFC-43-10mme and HFE-7100 or HFE 7200 all present themselves as highly qualified replacements for HCFC-141b. It is likely that HFC-43-10mme may most closely match the materials compatibility found with HCFC-141b but individual and very specific tests (with batches of actual components such as elastomer seals etc.) will have to be performed prior to putting any component into service. It may be that HFE-7100 / -7200 may also perform perfectly well in this regard, but the same caveats for specific tests apply. Of the two HFE compounds, HFE-7100 is the more attractive choice because has lower flammability (essentially zero), lower toxicity, and higher density.

One of the known, and oft-times over-emphasized characteristics of HCFC-141b is its ability to bind to ice chips and cause them to sink. It would appear that the mutual solubility with liquid water might be a good indication of this propensity to bind in the solid state. If that assumption holds true, then HFC-43-10mme and HFE-7100 /-7200 hold great hope for a drastic decrease in this problem (see water solubility data in the Table 2 , which follows below).

Laboratory tests for materials compatibility and physical characteristics will be required, including tests simultaneously at low temperature and high pressure to simulate borehole conditions. When HCFC-123 was suggested as a densifier it was laboratory tested only at low temperatures, it appeared to be suitable as a densifier; when put into service at NGRIP in 1999 it was found to bind aggressively to ice chips, forming a sinking slush (Gundestrup *et al*., 2002). The borehole had to be bailed and re-filled in zones with fluid using HCFC-141b densifier, which has been in use at NGRIP since that time.

Quantity and Cost of Drilling Fluid Required

There are several factors contributing to the overall cost of supplying drilling fluid for a given project. These include:

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[16] "mme" is an isomeric designation

- The volume of the borehole to be filled, obviously related to the overall depth and the diameter of the borehole
- Losses of fluid due to leakage
- Loss of fluid due to spillage
- Loss of fluid due to carry-out on slushy chips, which cannot be subsequently recovered via filtering, centrifugation, or melting
- Loss of fluid due to evaporation from core, and from wetted surfaces of the drill, cable and other contaminated surfaces
- Intrinsic cost of the fluid components, as purchased from the manufacturer
- Cost of transport to the site
- Engineering costs, associated with making equipment compatible with the fluid chosen
- Operating costs, including down-time, associated with regularly replacing components only marginally compatible with the fluid
- Cost of short-term compliance, and long-term liabilities, associated with health, safety, and environmental requirements imposed by the nature of the fluid(s) chosen, applicable laws, and self-imposed objectives.

Each of these is examined in more detail below.

Borehole volume is self-explanatory but must take into account the possible desire to ream the borehole to a larger diameter to accommodate faster tripping, and to increase the margin of safety once warmer ice is encountered (beyond, say, 2000 m depth). It must also include any deviation drilling (sidetrack) from the main borehole.

Loss due to fluid leakage is meant to include poor sealing at the bottom of the casing. Casing is installed to prevent fluid leakage and wicking into the firn zone. Were it not for the fluid issues, a casing would be required in any case, to prevent collapse of loose firn walls into the borehole.

Loss due to spillage is difficult to estimate, as it is of accidental nature; there will always be some losses of this type regardless of how careful the workers are.

Along with the ice core removed from the borehole, a nearly equal volume (or mass) of ice is removed in the form of fluid-soaked chips. Fluid is normally recovered from these chips by gravity drainage on filter screens followed by centrifugation.

More than 90-95% of the entrained fluid can be routinely recovered in this manner. The remaining absorbed or adsorbed fluid can only be removed by melting the ice and/or distillation. In either case, recovering that remaining fluid becomes an energy intensive and probably not cost-effective operation. One of the problems with melting the chips to recover fluid is the probability of distillation and loss of the higher vapor-pressure fluids. In two-component systems currently (or recently) in use, the higher vapor-pressure fluid being lost to distillation is the much more expensive densifier, so open-container melting makes little economic sense. It might only be justified in the presence of excess waste

heat from other sources (such as electrical generation) and / or an environmental mandate. Recovery of the volatile densifier compound(s) would require investment in a closed retort and condensation system.

A certain amount of fluid loss from ice-core surfaces is inevitable and must be accounted for. Strictly speaking, the thin film of fluid remaining on a 1-meter length of core after a short period of gravity drainage is not likely to exceed about 50 ml, so the average borehole loses only a couple of hundred litres of fluid directly in this manner. Much more fluid is lost due to inadvertent spillage on the floor, clothing, etc.

The intrinsic cost of the fluid(s) has been investigated and tabulated by Talalay and Gundestrup (1999); they reported that

- de-aromatized solvent (Exxsol^{TM} D-series fluids) cost about \$0.60/liter,
- HCFC-141b about \$5.00/liter and
- n-butyl acetate about \$0.80/liter.

Mixed to appropriate density, the two-component system {D-30 ~ 66% + HCFC-141b ~34%} was therefore about \$2 / liter.

Other HCFC's can cost more than ten times as much; for example in 1999, the price of HCFC-225a was reported to be about \$54.00/liter and is currently about \$65.00/liter. HFC-43-10mme currently costs about \$60 /liter, and HFE-7100 costs about \$56 / liter Even if all losses are neglected large quantities of fluid are required to fill the borehole: circa 50,000 liters for a 13-cm diameter hole or about 67,000 liters for a 15-cm diameter hole. It is then instantly obvious that the cost of the fluid is not insignificant.

The Table of Properties shows a rough estimate for the cost of enough fluid to fill one 50,000-liter borehole using NBA and each of the various workable-alternative densifiers mixed with D-40 to a density of 0.930 g/cc at room temperature. The exact ratio of mixing will be dependent upon more research into the compressibility and temperature-related expansion coefficients of the fluids. We can see that NBA is the lowest price alternative at about \$50k, and that potential two-component systems are an order of magnitude more expensive. The large initial investment must, however, be balanced against the drastic decrease in health and safety liabilities throughout the coring and core-handling system.

Allowance for losses requires that about 150% of the projected borehole volume should be budgeted for the overall fluid requirement (see, for example, Eustes *et al.,* 2003).

Transportation costs remain virtually fixed regardless of the fluid chosen. Fluid composition might become an issue if the fluid chosen was dangerous (highly toxic, explosive, etc.), requiring specialized handling, but this case is to be entirely avoided based on other considerations only.

A fixed transport cost should be obvious upon inspection, because the weight of the fluid to be transported is a function of the fixed volume of the borehole (and fixed rate of allowance for losses) and the fixed density required for hydrostatic compensation. The distance of transportation is likewise fixed by the location of the project site and nearest deepwater port; the cost of transport by sea to that deepwater port vanishes by comparison to other costs.

Fluid transportation cost will be influenced by choices made by logistical management (overland traverse vs. airlift). Significant savings are likely to be realized by establishing the project location early, and employing overland transport of the fluid and other bulk material in advance of the project, if possible.

Engineering costs associated with the fluid choice include time required to investigate, in theory and in practice, the compatibility of the fluid with various components. NBA and density-adjusted petroleum solvent both present such technical hurdles.

NBA is well known for attacking synthetic substances. Talalay and Gundestrup (1999, 2002a), taking exception to Gosink *et al.* (1991), noted that there are no elastomer compounds that can withstand NBA for long periods of exposure. Very low temperatures probably slow the attack, but this effect is probably not reliable from an engineering standpoint and doesn't protect components that have been saturated with NBA at low temperatures and subsequently exposed to warmer conditions - such as during storage, or for repairs, etc.

Choosing construction materials simultaneously resistant to

- The primary (first-choice) borehole fluid,
- An alternative borehole fluid that might be the best choice for unusual circumstances such as a temperate glacier,
- Antifreeze solutions that might be employed for emergency un-sticking of the drill (ethylene glycol + water, for example) and, finally,
- Internal compounds to be isolated from the drill fluid, such as lubricants,

will not be an easy task and may involve compromises. Some of these compromises may mean decreased reliability and a program of regular component replacement. Under some circumstances this may mean the provision of spare modules. Modules would be swapped out, inspected, and retrofitted with new seals (etc.) off-line to limit drilling down-time.

The cost of compliance with health, safety, and environmental requirements are not easy to assess. Order-of-magnitude costs can only be arrived at if higher authorities establish project management guidelines. For example, if a qualified industrial hygienist is hired to professionally assess the hazards presented to workers in the field and in the laboratories where ice cores are handled, that will add a fixed cost. On the other hand, provision of a hygienist or technician to do *daily* on-site monitoring, documentation, and safety equipment maintenance will be an on-going cost for the life of the project(s).

The nature of the fluid (or the fluid*s* in a two-component system) influences the requirements for ventilation, fire, and explosion-hazard abatement. Firstly, a time-weighted maximum exposure concentration has to be established and accepted, and, for a margin of safety, this must be *much lower* than the LEL. It is likely that the TWA limits will be far less than the explosive limit, but the setting of the desired TWA should be influenced by a frank admission that the staff averages a far-longer-than 8-hour-per-day exposure interval

Estimation of the evaporation rate of the fluid(s) at the projected ambient temperature (a function of wetted surface area, surface roughness, turbulence, air speed, temperature, and ambient air pressure), the room volume, etc. would be required for rigorous engineering analysis and this is unlikely to be carried out. Accept for comparison purposes that the EPICA program, using Exxsol^{TM} solvents and HCFC-141b as a densifier, operates with a ventilation rate of about 250 cubic meters per minute; efficiency is maximized because contaminated air is drawn from low-lying points and nearest the sites of maximum fume generation. Ventilation probably consumes about 3 or 4 kW of power or about 4% of total available generation capacity for these EPICA projects. Ventilation must be continuous while the camp is occupied. Use of a lower vapor pressure, low-toxicity compound such as HFE-7100 will further reduce ventilation requirements and sensitivity to ventilation failure as might occur due to electrical power outages.

The cost of environmental compliance is difficult to ascertain at this point. One may view the move from relatively inexpensive HCFC-141b, to a compound that has lower (or zero) ODP, as being an environmental cost.

Environmental costs lie largely within the logistics umbrella; the liabilities include transportation of fluid to and from the site, cleaning up the site following completion of operations, long-term monitoring, and possibly recovery of the fluid in the future.

Conclusions and Recommendations

Previous US programs involving n-butyl acetate as a drilling fluid. NBA has low initial purchase cost, but is an ongoing liability from a safety (fire and explosion), acute- and chronic-health-hazard standpoint. In stark contrast, the European drilling fluid system comprised of two components that were
- Low-toxicity,
- Workplace-safe,
- Engineering-materials-compatible, and
- Relatively inexpensive,

is an appealing alternative. The EPA production-and-import ban on HCFC-141b, which was the densifier used in the most recent European projects including NGRIP and EPICA, requires us to make intelligent choices.

We could continue to employ NBA as the US program has done in the past, or investigate a new dual-component fluid system. There appears to be a strong and rational ground swell of support for the abandonment of NBA as a drilling fluid, based on previous experiences. The new compounds, HFC-43-10mme and HFE-7100, marketed to replace HCFC-141b in various industrial applications, are the strongest contenders for the role of densifier in the WAISCORES project. Large samples of these compounds should be procured, and a testing program tailored to our application initiated, as soon as possible.

Accurate and precise pressure-logging tools must be available once drilling operations begin, to confirm the borehole fluid pressure as a function of depth and ascertain whether compensation is likely to exist. It must be remembered that the temperature (and therefore density and "lithostatic" pressure) within the glacier at WAISCORES is now only estimated; it is not yet known as fact.

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	n-Butyl Acetate	Exxsol D-40
Density, g/cc	0.880 @ 20 C	0.771 @ 15.6 C
Molecular Weight	116.6	141
Freezing Point	minus 77 C	< minus 60 C
Boiling Point	126	159 to 194 C (typically)
Vapor Pressure	1.07 kPa @ 20 C	0.289 kPa @ 20 C
Auto-Ignition Temperature	425 C	232 C
Flash Point	24 C (closed cup)	42 C
Lower Expl. Limit	1.20%	1.40%
Upper Expl. Limit	7.50%	8.90%
Vapor Density (Air = 1.0)	4	5
Relative Evap. Rate (NBA=1.0)	1	0.2
Kauri-Butanol Value (KB)		33
Kinematic Viscosity	0.72 cSt @25 c	1.28 cSt @25 C
TWA -8 hour / organization	150 ppm (OSHA) 200 ppm STEL; 30 ppm DECOS	197 ppm (Exxon)
LD50 (rat)	10.8 g/kg (rat)	> 5g/kg (oral, rat)
Exposure Route	Inhalatioin, skin and eye contact; accidental ingestion; IDLH at 1700 ppm inhalation	Skin contact, inhalation of vapor or mist
Irritating to…..	Eye (300 ppm human); skin	Eyes, respiratory tract
Carcinogenicity	Data for *in vivo* long term mutagenicity not available (DECOS)	Tumorigen (Limited Animal Evidence) RTECS OA5504000
Mutagenicity	(see comment above)	N/R
Reproductive Effects	Fetotoxicity, developmental defects; DECOS recommended further study in this area	N/R
Other Effects	CNS effects; change in brain and other organ weights, metabolic effects, altered RBC-count ; effects exacerbated by ethanol consumption; aggravates pre-existing kidney liver and respiratory disorders	Skin exposure may cause dermatitis
Aquatic Toxicity	"Moderately Toxic to Aquatic Life"	(low)
Ozone Depletion Potential (ODP)	N/A	
Global Warming Potential (GWP)	N/R	N/R
Solubility of Compound in water	8000 ppm	
Solubility of Water in Compound		
Materials Compatability	Most metals, teflon, many types of hard plastics, some elastomers are reasonably resistant.	Metals, most hard plastics and many elastomers; not highly aggressive
Materials Incompatability	Highly aggressive solvent, dissolving most coatings (paint, varnish, etc.), elastomers, plastics, etc. Compatability should be established by specific tests.	
Cost per liter	~$1.00	$0.54
% D-40 : % Densifier, v/v, for Fluid of Density 0.93 @ ~20-25 C	Used Neat (100%)	Varies (see notes under each Densifier)
Cost for 50 cu. meters of Drill Fluid (D-40 Base Stock + Densifier Compound)	$50 K	Not Used Alone
Conclusion	Poses significant safety and engineering challenges. May require some densifier for fine-tuning of balance point	One of several very similar hydrocarbon fluids with low toxicity and low cost, for use as dual-component system base-stock (Isopar K is only $0.65 / liter)

Table 2 (continued next page…)

	HCFC-225 ca/cb	N-propyl bromide
Density, g/cc	1.55 @25 C	1.32 @ 25 C
Molecular Weight		123
Freezing Point	minus 131	minus 110 C
Boiling Point	54 C	71 C
Vapor Pressure	37.72 kPa	14.6 kPa @20 C
Auto-Ignition Temperature		490 C
Flash Point	None	20 to 23 C
Lower Expl. Limit	N/R	4.00%
Upper Expl. Limit	N/R	8.00%
Vapor Density (Air = 1.0)		4.3
Relative Evap. Rate (NBA=1.0)	90	<1.0
Kauri-Butanol Value (KB)		126
Kinematic (Dynamic) Viscosity	1.18 cSt	
TWA -8 hour / organization	100 ppm (Federal Register; V.67, No. 56, p. 13275)	25 ppm (manuf.'s TWA)
LD50 (rat)		2.76 g/kg (rat, oral)
Exposure Route	Skin, Inhalation, accidental ingestion	skin, inhalation, ingestion
Irritating to…..	At high concentrations causes liver enlargement in the rat but only marginal effect in primate subjects (PAFT)	Highly irritating to skin, eyes, mucous membranes and respiratory tract at fairly low concentrations
Carcinogenicity	N/R	Not reported / Limited data / Similar compound n-butyl bromide and other alkyl bromides are suspected carcinogens
Mutagenicity	Neither isomer is genotoxic (PAFT)	in vitro studies show mutagenicity
Reproductive Effects	N/R	Potentially toxic to animal reproduction
Other Effects	Known to be a cardiac adrenaline-sensitizer, but only if the level of exposure is extreme (> 15,000 ppm)	Demonstrated neurological effects in rats
Aquatic Toxicity	N/R	No chromic exposure data available
Ozone Depletion Potential (ODP)	0.03	<0.026
Global Warming Potential (GWP)	180 for ca isomer, 45% v/v ; 620 for cb isomer, 55% v/v (Weighted Average 370)	0.31
Solubility of Compound in water	330 ppm	2500 ppm
Solubility of Water in Compound	310 ppm	
Materials Compatability	Common metals; PTFE, EPDM and chloroprene elastomer seals	Dissolves in ethanol, acetone and chloroform but may not be highly soluble in aliphatic hydrocarbons such as D-40
Materials Incompatability	Acrylic resin plastics, some polycarbonate, some types of ABS	Hydrolyzes on water contact to form acid
Cost per liter	~ $65.00	See Note Below
% D-40 : % Densifier, v/v, for Fluid of Density 0.93 @ ~20-25 C	80.3% : 19.7%	Not Suitable For This Application
Cost for 50 cu. meters of Drill Fluid (D-40 Base Stock + Densifier Compound)	$680k	Not Suitable For This Application
Conclusion	Will eventually be banned as a Montreal Protocol Class II ozone depleting substance beginning no later than 2015 and to be completely out of the market place by 2030. It doesn't make sense to begin a new drilling application with that fact in mind	Suitable only in closed-system applications. Atofina Corporation calculated an 8-hour OEL of under 5 ppm which would be "difficult to maintain in open-solvent conditions" and therefore refuses to market the product for this application

Table 2 (continued)

	HFC-43-10mme	PFC "FC-87"
Density, g/cc	1.58 @ 25 C	1.65 @ 25 C
Molecular Weight	252	288
Freezing Point	minus 80 C	< minus 115 C
Boiling Point	55 C	30 C
Vapor Pressure	30.12 kPa	81 kPa
Auto-Ignition Temperature	>300 C	Not Applicable
Flash Point	none	none
Lower Expl. Limit	None	none
Upper Expl. Limit	None	none
Vapor Density (Air = 1.0)	> air	~ 10 @ 20 C
Relative Evap. Rate (NBA = 1)		" > 1.0"
Kauri-Butanol Value (KB)		
Kinematic (Dynamic) Viscosity	~ 0.42 cSt (0.67 centipoise)	0.27 cSt (25 C)
TWA -8 hour / organization	200 ppm; 400 ppm Ceiling (Manu.)	None established-- considered to be very low hazard
LD50 (rat)	> 5g/kg (rat, oral)	
Exposure Route	skin; inhalation of mist or vapor	Inhalation, Skin
Irritating to…..	skin and eye irritant	Insignificantly irritating to skin or eyes
Carcinogenicity	N/R	N/R
Mutagenicity	N/R	N/R
Reproductive Effects	N/R	N/R
Other Effects	Cardiac Adrenalin Sensitizer; Increased sensitivity and/or risk for those with pre-existing disease conditions	N/R
Aquatic Toxicity	low	very low
Ozone Depletion Potential (ODP)	0	0
Global Warming Potential (GWP)100-year Integration Time Horizon (ITH)	1300	5000
Solubility of Compound in water	140 ppm	7 ppm w/w
Solubility of Water in Compound	490 ppm	< 5 ppm w/w
Materials Compatability	Short term compatibility with most plastics. Long term compatibility by investigation; affected by content of plasticizer agents etc.	Most metals and plastics including sensitive materials; specific tests of materials should be carried out
Materials Incompatability	Elastomer swelling or shrinkage	Softens or Dissolves Fluorinated compounds; Immiscible in Hydrocarbon Fluids
Cost per liter	$59.30	$127.00
% D-40 : % Densifier, v/v, for Fluid of Density 0.93 @ ~20-25 C	81% : 19%	Not compatible with Petroleum Base Fluid
Cost for 50 cu. meters of Drill Fluid (D-40 Base Stock + Densifier Compound)	$560k	Not Applicable: Immiscible with Hydrocarbons Solvent
Conclusion	Should be investigated as a potential densifer for WAISCORES project	Not suitable for this application

Table 2 (continued)

	HFE-7100	HFE-7200
Density, g/cc	1.52 @ 25 C	1.43 @ 25 C
Molecular Weight	250	264
Freezing Point	minus 135 C	minus 138 C
Boiling Point	61 C	76 C
Vapor Pressure	21.7 kPa @20 C	14.5 kPa @ 25 C
Auto-Ignition Temperature	405 C	375 C
Flash Point	None	Not Applicable
Lower Expl. Limit	None	210 g/cubic meter
Upper Expl. Limit	None	1070 g / cubic meter
Vapor Density (Air = 1.0)	8.6	9.1
Relative Evap. Rate (NBA = 1)	49	33
Kauri-Butanol Value (KB)	~10	~10
Kinematic (Dynamic) Viscosity	0.37 cSt @ 25 C	0.43 cSt
TWA -8 hour / organization	750 ppm (AIHA WEEL)	200 ppm (manu.)
LD50 (rat)		
Exposure Route		
Irritating to…..	Not significantly irritating to eyes or skin	Not significantly Irritating to Eyes or Skin
Carcinogenicity	N/R	N/R
Mutagenicity	N/R	N/R
Reproductive Effects	N/R	N/R
Other Effects	N/R	Single Observed Case of Cardiac Sensitization at > 49,000 PPM
Aquatic Toxicity	Insignificant	Insignificant
Ozone Depletion Potential (ODP)	0	0
Global Warming Potential (GWP)100-year Integration Time Horizon (ITH)	320	55
Solubility of Compound in water	< 12 ppm	< 20 ppm
Solubility of Water in Compound	95 ppm	92 ppm
Materials Compatability	Most metals and plastics including sensitive materials; specific tests of materials should be carried out	Most metals and plastics including sensitive materials; specific tests of materials should be carried out
Materials Incompatability	Will be absorbed into fluorinated plastics and elastomers, given long exposure time	Will be absorbed into fluorinated plastics and elastomers, given long exposure time
Cost per liter	$56.00	$56.00
% D-40 : % Densifier, v/v, for Fluid of Density 0.93 @ ~20-25 C	79% : 21%	77% : 23%
Cost for 50 cu. meters of Drill Fluid (D-40 Base Stock + Densifier Compound)	$612k	$681k
Conclusion	Should be investigated as a potential densifer for WAISCORES project; preferred over HFE-7200 due to higher density, good volatility, lowest toxicity, and even lower fire risk	Should be investigated as a potential densifer for WAISCORES project; HFE-7100 appears to be better choice based on present data

Table 2 (Continued)

	HFE-7500
Density, g/cc	1.61 @ 25 C
Molecular Weight	414
Freezing Point	minus 100 c
Boiling Point	130 c
Vapor Pressure	1.77 kPa @20 C
Auto-Ignition Temperature	332 C
Flash Point	none
Lower Expl. Limit	none
Upper Expl. Limit	none
Vapor Density (Air = 1.0)	14.3
Relative Evap. Rate (NBA = 1)	No Data Available
Kauri-Butanol Value (KB)	~10
Kinematic (Dynamic) Viscosity	0.77 cSt @ 25 C
TWA -8 hour / organization	Not established
LD50 (rat)	>2 g/kg
Exposure Route	
Irritating to…..	not significantly irritating to eyes or skin
Carcinogenicity	N/R
Mutagenicity	negative, in two assays conducted
Reproductive Effects	N/R
Other Effects	N/R
Aquatic Toxicity	Insignificant
Ozone Depletion Potential (ODP)	0
Global Warming Potential (GWP)100-year Integration Time Horizon (ITH)	100
Solubility of Compound in water	< 6 ppm
Solubility of Water in Compound	45 ppm
Materials Compatability	Most metals and plastics including sensitive materials; specific tests of materials should be carried out
Materials Incompatability	Will be absorbed into fluorinated plastics and elastomers, given long exposure time
Cost per liter	$102.00
% D-40 : % Densifier, v/v, for Fluid of Density 0.93 @ ~20-25 C	82% : 18%
Cost for 50 cu. meters of Drill Fluid (D-40 Base Stock + Densifier Compound)	$951k
Conclusion	Probably too viscous and vapor pressure too low for application to ice core drilling; cost is also significantly higher

Table 2 (end)

Glossary of Acronyms

ACGIH	American Council of Government and Industrial Hygienists
AIHA	American Industrial Hygiene Association
ABS	Acrylonitrile Butadiene Styrene (thermoplastic)
CAS	Chemical Abstract Services
CFC	Chlorofluorocarbon
CRREL	US Army, Cold Regions Research and Engineering Laboratory
DECOS	Dutch Expert Committee on Occupational Standards
DEW	[DEW-line] Distant Early Warning system of Arctic RADAR stations
DOT	U.S. Department of Transportation
DYE-3	Cape Dyer (Greenland), DEW-line Site Number 3
ECSA	European Chlorinated Solvents Association
EPA	U.S. Environmental Protection Agency
EPDM	Ethyl Poly Diene Monomer (Elastomer Compound)
EPICA	European Program for Ice Coring in Antarctica
GISP2	Greenland Ice Sheet Project #2
GRIP	GReenland Ice-sheet Project
GWP	Global Warming Potential (integrated effect over time, referenced to CO_2)
HCFC	Hydrochlorofluorocarbon
HDPE	High Density Polyethylene (a common type of plastic)
HFC	Hydrofluorocarbon
HFE	Hydrofluoroether
HMIS	Hazardous Materials Identification System
IDLH	Immediately Dangerous to Life or Health [Concentration]
ITH	Integrated Time Horizon (e.g., "100-year ITH") *see* GWP
JARE	Japanese Antarctic Research Expedition
JP	Jet Petroleum (Fuel)
Kb	Kauri Butanol (measure of solvent effectiveness)
L_C50	Lethal Concentration required to kill 50% of the exposed population
L_D50	Lethal Dose required to kill 50 % of the exposed population
LEL	Lower Explosive Limit [Concentration; *see* UEL]
MSDS	Material Safety Data Sheet
NBA	n-butyl acetate
NFPA	National Fire Protection Association
NGRIP	North GReenland Ice-sheet Project
NIOSH	National Institute for Occupational Safety and Health
NPB	n-Propyl Bromide
ODP	Ozone Depletion Potential
ODS	Ozone Depleting Substance
OSHA	Occupational Safety and Health Administration
PAFT	Programme for Alternative Fluorocarbon Toxicity Testing
PEL	Permissible Exposure Limit
PICO	U.S. Polar Ice Coring Office
PTFE	Polytetrafluoroethylene (Teflon®)
RADAR	RAdio Detection And Ranging

RBC	Red Blood Cell (-count)
RTK	"Right to Know" (Legislation)
RTECS	Registry of Toxic Effects of Chemical Substances
s.l.	*Sensu lato*: in the broad sense of the word or phrase
SNAP	Significant New Alternatives Program (*of* U.S. EPA)
STEL	Short Term Exposure Limit
TWA	Time Weighted Average
UEL	Upper Explosive Limit [Concentration; *see* LEL]
US-EPA	See "EPA," above
VMS	Volatile Methyl Siloxane
WEEL	Workplace-Established Exposure Limit
WAIS	West Antarctic Ice Sheet (project)

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