

New hydrate inhibitors annual report 1997 for  
NFR

RF-1997/284-249

**New Hydrate Inhibitors  
Annual Report 1997 for NFR  
Report RF-97/284**

Our reference: <b>451-97/284</b>	Author(s): <b>Malcolm Kelland</b>	Version No. / date: <b>Vers. 1 / 28.11.97</b>
No. of pages: <b>4</b>	Project Quality Assurance. <b>Sigmund Stokka</b>	Distribution restriction: <b>Open</b>
ISBN:	Client(s): <b>NFR</b>	Open from (date):
Research Program:	Project title: <b>New Hydrate Inhibitors</b>	

**Scope:**

RF-Rogaland Research has identified low dosage hydrate inhibitors as "low volume chemical" replacements for traditional "high volume" hydrate inhibitors such as glycols and methanol.

During 1997 RF pilot tested one new class of "kinetic inhibitor." The cost and performance of the kinetic inhibitor was better than any previous class tested. The inhibitors have been patented by RF and environmentally tested. The supplier that RF is collaborating with has planned to make tonne quantities in 1998 for a field trial, probably in the North Sea. This new inhibitor should be available during 1999 for commercial use.

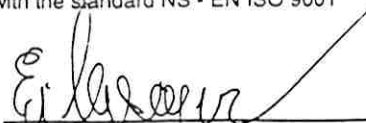
Two classes of a second type of low dosage hydrate inhibitor called "anti-agglomerator" have been identified, screened, patented and pilot tested. Further work is needed to optimise the performance and at the same time to keep the environmental impact as low as possible.

Key-words: hydrate, inhibitor, kinetic inhibitor, anti-agglomerator

RF - Rogaland Research has a certified Quality System in compliance with the standard NS - EN ISO 9001



Project Manager  
Malcolm Kelland



for RF - Petroleum  
Egil Bergsager

# 1 Introduction

The offshore oil and gas industry faces new technical and environmental challenges as we approach the next millenium. Two factors stand out as of crucial importance if the industry is to continue a high production level and personnel activity. These are:

- reduction of discharged chemicals to the North Sea (viz. Miljøsoek)
- cost-effective solutions to develop small marginal fields and sub-sea tie backs, especially in cold or deep water.

Controlling hydrate formation is a major challenge in these respects. A plug in a well or pipeline due to hydrate formation can cost the operator millions of dollars. In extreme cases the pipeline has to be cut out and replaced (e.g. the UK Staffa field, operated by Lasmo). Downhole or subsea separation techniques will never be able to remove all the water, so hydrates will always be a hazard to avoid for operators. Alternative non-chemical methods to avoid hydrate formation and plugging of lines are very expensive. Various bundles or pipe-in-pipe heating techniques cost \$1-4 million per km or line. This cost is unfeasible for small fields or medium size fields in deepwater with long tiebacks. Therefore, chemical treatment will remain a major method to avoid hydrate formation.

In order to help Norway reduce the large quantities of methanol and glycols used offshore today, alternative low dosage chemicals are required. These chemicals would be used at less than 0.5 wt. % of the water phase i.e. at about 1/100 the concentration of methanol and glycols. Clearly, the use of the new inhibitors would be a good way to reduce chemical discharge.

The difficulties in developing the low dosage inhibitor technology are four fold:

- environmentally-acceptability (SFT discharge regulations and OsParcom)
- cost (of the whole treatment, not just the chemical cost)
- performance
- compatibility (to field conditions, other production chemicals and process facilities)

Two methods of inhibition have been identified which lead to the definition of two classes of low concentration hydrate inhibitors:

1) Inhibitors which delay kinetically the hydrate formation process - called **Kinetic Inhibitors (KI)**.

2) Inhibitors which disperse the hydrates to form a transportable non-plugging slurry - called **Anti-Agglomerants (AA)**.

## 2 Progress in Kinetic Inhibitor Development in 1997

Kinetic inhibitors (KIs) are already being used offshore in the UK Southern North Sea gas fields as well as several other locations around the world particularly on-land in the USA. Next year, the large Eastern Trough Area Project (ETAP) in the UK North Sea will use KIs. BP has calculated that this has given BP a CAPEX saving of \$45 million over the alternative use of methanol.

The progress milestone approved by the members of this project for 1997 was to develop an offshore acceptable KI which had the following performance:

*Prevent total hydrate formation at 15°C in oil-water-gas mixtures at up to 90 bar.*

This has been achieved both in laboratory and pilot testing at Petreco.

KIs already available today have several drawbacks which will restrict their application range in their future:

- subcooling performance limitations
- cloud point compatibility at wellhead injection point
- non-biodegradability
- cost

RF has addressed all of these issues throughout this joint industry project. In 1997 we took two classes of inhibitor, previously identified in 1995-96, and carried out optimisation studies to meet these offshore requirements as well as pilot testing of one class of KI. We found that by optimising the structure (molecular modelling studies in UK) we could obtain better performance than any previous inhibitor tested. Secondly, we managed to optimise the structure to get the cloud point high without losing performance. This makes the inhibitor able to be injected at hot wellheads without danger of deposition. Thirdly, we managed to optimise the structure to give low toxicity values and high water-solubility such that the bioaccumulation  $\log P_{ow}$  is less than 1. The SFT states that chemicals with biodegradation  $BOD_{28} < 20\%$  and simultaneously have bioaccumulation  $\log P_{ow} > 5$  will not be accepted for offshore discharge. The SFT also recommends that operators try to priorities replacing chemicals with  $\log P_{ow} > 3$ , with a priority ranking dependent on the percentage biodegradability. Although the KI product RF has developed is not inherently biodegradable ( $BOD_{28} < 20\%$ ) it does degrade slowly over time. More importantly, since it has such low toxicity and bioaccumulation, the product is expected to fall in a low priority category (Cat. 4) of chemicals that the SFT would like to see replaced. Finally, the cost of this KI product is expected to be considerably less than KIs used today.

The supplier of this KI, with whom RF has a collaboration, will be producing the chemical in tonne quantities in 1998. RF is planning a field trial next year with this chemical, possibly at the Tommeliten field (Statoil operated) if it doesn't close due to economic reasons. The product should be commercially available in 1999.

RF also discovered during 1997 a second class of KI which have high tolerance to high salinity brines. Such brines are found on many high temperature fields such as Åsgard.

During the latter part of 1997, RF explored possibilities to manufacture KI products but with ready biodegradability. Two suppliers were identified who could make prototype chemicals for testing and collaboration agreements were put in place. RF hopes to develop readily biodegradable hydrate inhibitors in future work (Phase 2).

### **3 Progress in Anti-Agglomerants (AAs) Development in 1997**

AAs are needed for high subcoolings, shutdown/start-up situations and deepwater applications where kinetic inhibitors cannot perform sufficiently. The focus in 1997 in this project moved more from KIs to AAs as the limitations of KIs became clear.

Shell was the first to develop an AA, but ran into a problem in 1997 when their chemical was turned down by the SFT for a field trial. The chemical is a quaternary surfactant, structurally related to known biocides and is therefore rather toxic. As all Shell's products are related to biocide chemicals, the prospect of finding an environmental-acceptable product from the Shell technology is probably slim.

The progress milestone approved by the members of this project for 1997 was to develop an AA which had the following performance:

*Prevent deposition of hydrates and no torque changes in laboratory tests using oil-water-gas at up to 90 bar and down to 3°C.*

This has been achieved in laboratory testing as requested.

This project has specifically addressed the needs for environmental-acceptable AAs for hydrate control. Several products were identified during 1995-6 from molecular modelling and screening work. These products were environmentally tested in 1997 as well as pilot tested. What we learnt from this work was as follows:

1. It is difficult but a tough challenge to develop an environmentally acceptable AA.
2. The shutdown/start-up test procedure in the laboratory does not always correlate with the pilot test results.
3. We have a much better understanding of the AA mechanism which has helped us in designing AA structures.

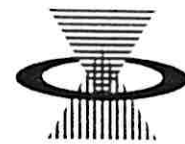
At present, we have pilot tested 3 new classes of AAs at Petreco which were initially screened at RF. We believe it will be difficult with at least one of these classes to find a low toxicity molecule although the bioaccumulation can be made low and the biodegradation high. Therefore, it is necessary to optimise the structures of the other two classes to find an environmentally acceptable AA which retains the required performance at an affordable cost. We are continuing to work with two outside suppliers on this. The rewards are huge as today there are no cheap methods to solve the hydrate problem in deepwater and tied-back subsea developments.



Norges  
forskningsråd

## Årsrapport 1997

Prosjekt/seksjonsnr:	ENERGI 32453/211		
Prosjektittel:	New Hydrate Inhibitors		
Program:	UTBYGG		
Kontraktspartner, navn og adresse:	Prosjektleder:	Malcolm Kelland	
	Foretaksnr.:	950 884 800	
<b>RF - Rogalandforskning</b>	Bankgiro:	3201.05.12963	
<b>Postboks 2503, Ullandhaug</b>	Telefon:	51 87 50 00	
<b>4004 Stavanger</b>	Telefax:	51 87 52 00	
<b>Resultatdokumentasjon</b> Dersom det i perioden er fremkommet et delresultat som kan belyse prosjektets nytteverdi, skal dette beskrives på maksimalt 10 linjer. Beskrivelsen må være i en enkel journalistisk form egnet for offentliggjøring i Forskningsrådets årsberetning, informasjonsblad o.l.			
<p>RF-Rogaland Research has identified low dosage hydrate inhibitors as "low volume chemical" replacements for traditional "high volume" hydrate inhibitors such as glycols and methanol.</p> <p>During 1997 RF pilot tested one new class of "kinetic inhibitor." The cost and performance of the kinetic inhibitor was better than any previous class tested. The inhibitors have been patented by RF and environmentally tested. The supplier that RF is collaborating with has planned to make tonne quantities in 1998 for a field trial, probably in the North Sea. This new inhibitor should be available during 1999 for commercial use.</p> <p>Two classes of a second type of low dosage hydrate inhibitor called "anti-agglomerator" have been identified, screened, patented and pilot tested. Further work is needed to optimise the performance and at the same time to keep the environmental impact as low as possible.</p>			
Har forskningsarbeidet utført i perioden avvik i forhold til kontraktfestet arbeidsplan?			
Ja <input type="checkbox"/> Nei <input checked="" type="checkbox"/>			
Periodens kontraktfestede delmål / milepæler er nådd:			
Ja <input checked="" type="checkbox"/> Nei <input type="checkbox"/>			
Nærmere redegjørelse for status og avvik er gitt på de etterfølgende sider (som alle er merket med prosjektnr og -tittel). Rapportering følger den disposisjon som er spesifisert på baksiden av dette skjemaet.			
Dato:	28/11/97	Prosjektleder:	<i>M. Kelland</i>



Norges  
forskningsråd

## Resultatrapportering 1997

Prosjekt-/seksjonsnr.: 32453/211  
Prosjekttittel: New hydrate inhibitors  
Program: UTBYGG

Utfylt av/dato: MALCOLM KELLAND 28/11/97

	T.o.m. 1996*	1/1-31/12 1997	Forventet senere i prosjektperioden Phase 2
Antall nye produkter ferdigstilt	0		2
Omsetning fra nye produkter (1.000 kr)	0		40.000
Antall nye prosesser ferdigstilt	0		2
Kostnadsbesparelser fra nye prosesser (1.000 kr)	0		100.000
Antall bedrifter som har tatt i bruk ny teknologi fra prosjektet	0		8
Antall bedrifter etablert på grunnlag av prosjektet	0		
Registrerte patenter	0 2	5	1
Lisenskontrakter	0		2
Dr.grad igangsatt i alt	0 1	1	
- herav kvinner	0		
Dr.grad avlagte	0		2
- herav kvinner	0		0
Artikler i vitenskapelige tidsskrifter med referanseordning	0		
Artikler i fagtidsskrifter/rapporter	0 1	1	1
Bøker (monografier mv.)	0		
Foredrag på internasjonale fagkonferanser	0 1	1	2

\*Forhåndsutfylt basert på Resultatrapportering 1996. Før på evt. endringer!

(Fylles ut av Forskningsrådet) Godkj. av programkoord., sign./dato: \_\_\_\_\_

Norges Forskningsråd  
Stensberggata 26  
PO Box 2700 St. Hanshaugen  
N-0131 Oslo



Att: Torbjørn Fidtje

Your ref.

Our ref.  
451/mak/br

Stavanger  
November 28, 1997

Ref. 32453/211: Utbygg Programme

**Annual Report on "New Hydrate Inhibitors" Project**

Please find enclosed the 1997 annual report for the joint industry project "New Hydrate Inhibitors."

Yours sincerely  
RF - Rogaland Research

Malcolm Kelland  
Group Supervisor  
RF-Petroleum

Enclosures: Annual report