RECLAMATION/REGENERATION OF GLYCOLS USED FOR HYDRATE INHIBITION

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Abstract

The use of ethylene glycol for hydrate inhibition in gas production lines is well established and works effectively as long as the salt solubility is not exceeded. Offshore deepwater gas production presents a problem of salt contamination due to hydrate inhibition requirements in subsea production lines carrying gas, condensate, and brine.

An offshore production system experienced a number of problems due to brine contamination. The problems were resolved using the patented CCR process, initially thru the use of an onshore trailer mounted process, and ultimately a module was installed offshore.

CCR Technologies Inc. has proven, proprietary technology for the reclamation and regeneration of contaminated MEG used as a hydrate control chemical for offshore deepwater gas production facilities. This patented technology overcomes problems experienced with earlier attempts at salt contaminated glycol regeneration. Salt laden MEG is processed reliably, equipment fouling is virtually eliminated, and clean MEG is regenerated for re-injection as hydrate control chemical. Recovery factors are high, which reduce glycol chemical costs and allow an economical solution for deepwater hydrate control.

A description of the process and operating experience will be detailed.

Subsea Developments – Flow Assurance

Many of the deepwater fields will be developed as subsea completions with production either tied back to a host platform in shallow water or pipelined to a floating production system e.g. a SPAR, FPSO, semisubmersible, or TLP. Although subsea-processing equipment to separate production fluids is now being developed and tested, subsea flowlines transporting the entire wellstream to the host facility are expected to be used for the foreseeable future. In many cases the host processing facility will be remotely located, possibly many miles from the producing wells. Therefore, flow assurance in the gas gathering system becomes a critical issue in all subsea deepwater developments. Sea bottom temperature in the deepwater is cold, often near or below $40^{o}F$, even in equatorial waters. Cooling of wellstreams during transportation can lead to precipitation of troublesome hydrates and other solids such as waxes and asphaltenes. These solids can plug flowlines and other subsea equipment and their removal is often achieved only at significant cost.

Natural Gas Hydrates

Hydrates are a physical combination of water and other small molecules (e.g. the light hydrocarbons methane through n-butane, CO_2, N_2 and H_2S) to form a solid material having an "ice-like" appearance but with significantly different structure and properties than ice. For example, hydrates in gas systems containing high concentrations of H_2S can form at temperatures exceeding $90^{o}F$.

Hydrates have been a longstanding problem in the gas industry (reference: Hammerschmidt's 1934 paper "Formation of Gas Hydrates in Natural Gas Transmission Lines"). The primary factors influencing hydrate formation include:

- The fluid must be at or below its water dew point (i.e. must be water-saturated)
- Temperature
- Pressure
- Composition

Other considerations for hydrate formation include mixing, kinetics (hydrate formation is a time dependent process), type of physical site and surface for crystal formation and agglomeration and the salinity of the system. In general, hydrate formation will occur as system pressure increases and/or temperature decreases to formation conditions.

The principle by which alcohols, glycols and salts inhibit hydrates is the same. A substance soluble in the aqueous phase competes for the water molecule or ion and prevents the water from forming solid hydrates with the hydrate forming constituents in the gas or non-aqueous liquid phase. To inhibit hydrates, a minimum concentration of the solute or inhibitor is necessary in the solvent or aqueous phase. Various empirical methods, charts and computer programs have been developed to predict hydrate formation and inhibition.

New classes of compounds are being developed such as kinetic inhibitors that slow the rate of hydrate formation and anti-agglomerators, which prevent the hydrates from agglomerating and

forming plugs. These chemicals show promise and are now being developed and field-tested, but none are presently known to be in service for the severe hydrate formation conditions found in subsea gas systems.

Subsea Hydrate Inhibition Options

The hydrate inhibition method selected must ensure hydrates will not form, or the hydrates remain transportable during steady state, transient and shut-in conditions. Traditional techniques to avoid hydrate formation are achieved by conservation and/or input of heat, or lowering the temperature at which hydrates form through the addition of thermodynamic inhibitors. Heat conservation can work during steady state conditions but can be of no benefit in certain transient or shut-in scenarios. Heat input in onshore gas gathering/transmission systems (e.g. installation of line heaters) might not be applicable to subsea production systems. Also, depending on location of a hydrate plug, some of the techniques to remediate onshore hydrates (e.g. line depressurization) might not be possible on long, high pressure, deepwater subsea flowlines. Heated and insulated (e.g. pipe-in-pipe) flowlines can be feasible for some subsea applications depending upon the fluid being transported, the tieback distance, and topsides capabilities of host platform.

In most subsea applications, hydrate formation will be controlled by injection of a chemical hydrate inhibitor, and the inhibitor selection process often involves a choice between either a glycol (usually MEG) or methanol. Inhibition by injecting salt solutions (e.g. NaCl or $CaCl_2$ brine) can provide some hydrate temperature suppression, but normally this alone is not sufficient to avoid hydrates in the cold deepwater environment. Likewise, the salinity of any brine produced with the oil and gas will generally not be adequate to inhibit the gathering system.

A selection of either MEG or methanol for deepwater hydrate inhibition involves comparison of many factors including capital and operating costs. Certain site-specific conditions, e.g. flowline operating temperature and pressure, or an operator's previous favorable or unfavorable experience might also influence the selection process. Both chemicals are deepwater proven and can provide the necessary inhibition in a properly designed system. A primary factor in the selection process is whether or not the spent chemical will be recovered, regenerated and reinjected. Glycol is normally recovered and recycled, whereas, methanol is used in both once-through systems and in some cases partially recovered. The operating cost for chemical makeup can become very significant in a once-through methanol system, particularly for high gas and/or produced water rates.

The decision to install a regeneration system is driven by an economic trade-off between capital expenditures vs. operating expenses. Although once-through methanol is used in many Gulf of Mexico subsea fields, in this case the expected low volume of produced water resulted in a methanol injection rate greater than for glycol. This is due to the high solubility loss of methanol into the gas phase at subsea pipeline conditions. Any methanol distributing to the gas phase is ineffective in inhibiting hydrates. Without recovery facilities, the large makeup volumes of methanol required to inhibit the high volume of gas would represent an extremely high operating cost. As shown in Figure 1 even with expensive methanol recovery and regeneration facilities,

the makeup requirements for methanol lost into the sales gas would represent a large operating expense. This methanol is lost to the gas phase, and hence unrecoverable even with a methanol recovery unit.
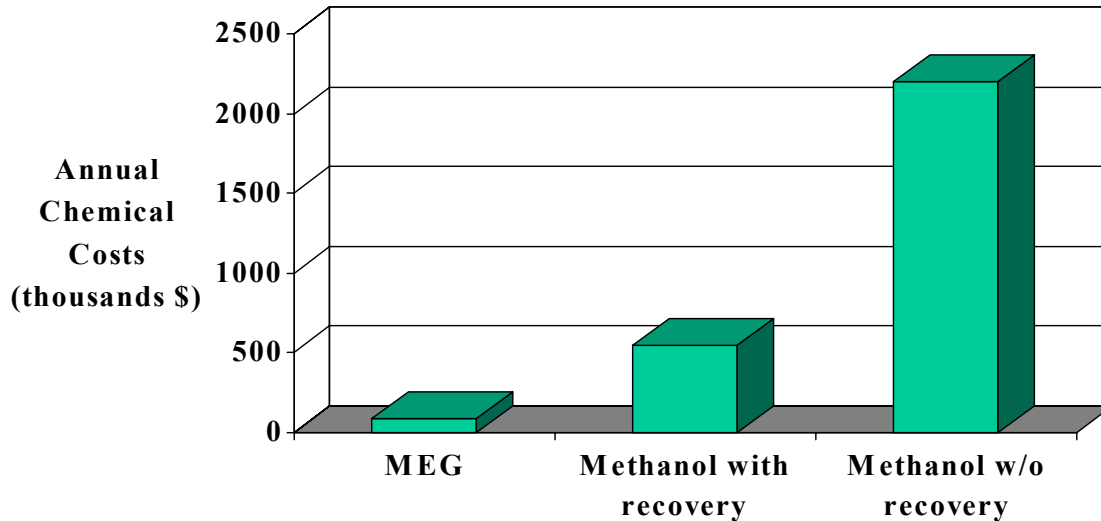

Figure 1 Expected Annual Chemical Costs for Hydrate Inhibition Alternatives

Other selection criteria to be considered include:

- Gas Dehydration Capability – Methanol will not dehydrate gas to pipeline specification (typically 7 lb/MMSCF). MEG and the other glycols have this capability that eliminated the requirement for a TEG contactor on the topsides.

- Chemical Cost – Methanol is less expensive per gallon than MEG although its price varies significantly. The price of MEG is fairly stable. The controlling factor is the product of chemical cost times gallons consumed, thus chemical losses rather than price per gallon can have the greatest bearing on chemical costs.

- Physical Properties – The viscosity of methanol is at least an order of magnitude less than that of MEG, thus reducing the pressure drop and pumping horsepower required for injection. The lower molecular weight of methanol (32 versus 62 for MEG) allows more dilute methanol solutions to be used since hydrate temperature depression is a molar phenomenon. However the amount of methanol in the gas phase must be also considered when calculating methanol injection rates.

- Safety – Methanol poses greater safety risks in handling and storage than MEG. For example, flash points of methanol and MEG are 52 and 232°F, respectively.

- Corrosion Inhibition of Flowlines – Typically MEG provides a greater degree of corrosion protection than methanol.

- Solubility Losses – Solubility loss of MEG into the sales gas is negligible and loss to the liquid hydrocarbon phase is very low. Depending on operating conditions, the solubility loss of methanol into sales gas can be very high, typically 1 lb of methanol/MMSCF for every % methanol in water phase. Losses to the liquid hydrocarbon are higher than for MEG but usually less than 1-2% of hydrocarbon volume. Depending on solubility losses chemical makeup requirements for methanol can be very large and expensive for both once-through systems and methanol recovery units.

- Tolerance to Salts – Both methanol and glycol solutions can become contaminated with salts. In recovering methanol by distillation, any salts present distribute to the aqueous phase since methanol is more volatile than water. The reverse is true when regenerating glycol. Since water is more volatile than glycol the salts remain behind in the glycol phase during regeneration. To avoid salt precipitation and plugging problems, it will be necessary to remove salts from the glycol solution.

- Paraffin Inhibition – MEG has paraffin inhibition/dispersion properties while methanol has at best exhibits very little inhibition properties. MEG if present in sufficient quantities relative to the volume of condensate or oil inhibits paraffin deposition by forming an aqueous continuous emulsion phase.

- Environmental Issues – Both MEG and methanol can contribute to toxicity of the overboard produced water discharge. In some overseas locations (e.g. North Sea) the methanol concentration of water discharged is limited to 1000 ppm maximum.

- Solid Waste – No solid waste is generated in methanol recovery processes. Glycol reclaiming processes can generate a solid or concentrated liquid waste product, primarily salt, for disposal.

- Downstream Issues – As previously stated a significant amount of methanol would be lost to the hydrocarbon phases, which may cause problems for the refineries and gas plants downstream. In gas plants where there is propane recovery the methanol will follow the propane product and potentially cause the propane to go off spec. Methanol has also been known to cause premature failure in mol sieves. In refineries the methanol must be washed out of the crude/condensate, where it presents a problem in wastewater treatment. For glycol systems there is virtually no loss to gas phase, and the solubility of glycol in the hydrocarbon liquids is typically 1 to 2 orders of magnitude less than methanol.

MEG Regeneration/Reclamation

When MEG is utilized for hydrate inhibition, it is nearly always recovered, regenerated and reused. At land locations, formation brine is usually separated from the gas near the wellhead and prior to injection of glycol. The separation step reduces salt contamination of the glycol. However, for subsea production systems, separation of produced water on the sea floor is not

normally possible and any salt water associated with produced gas will distribute into and be separated with the rich glycol phase.

Since salt is non-volatile, it will remain in the lean glycol during regeneration as the water is boiled off. If salt enters the glycol system with production fluids, either continuously or in periodic slugs, its concentration in the system will increase during each regeneration cycle until the solubility limit is finally reached and precipitation will then occur. Unless glycol is reclaimed by removing the salt, serious fouling and plugging of equipment and flowlines can result. Depending on the magnitude of the contamination problem, solvent reclamation can be accomplished either by continuous or intermittent (i.e. batch) removal from either the total circulation stream or else a partial slipstream.

Offshore Project

The project was a large subsea gas development in the Gulf of Mexico located approximately 140 miles southeast of New Orleans.

The gas is very lean, consisting of about 99.3% methane with only minor concentrations of other light hydrocarbon components, CO_2 and N_2. Before startup, it was anticipated that only negligible quantities of liquid hydrocarbon condensate and salt water would be produced in association with the gas. Since the gas is water-saturated at reservoir conditions, about 0.3 BBL/MMSCF of fresh water was expected to condense from the gas phase due to cooling in the cold deepwater environment.

Inhibition of hydrates is a critical issue for This project. For the gas composition and for a flowing wellhead pressure of 6000 psi, the estimated hydrate formation temperature is about $80^{o}F$. With seabed temperatures of $38-40^{o}F$ in deepwater, a hydrate point depression of $40-45^{o}F$ is required to avoid formation of these troublesome solids and the potential plugging of subsea flowlines and equipment.

Glycol and methanol were considered for the hydrate inhibition service. Glycol was selected for economic reasons, reducing capital expenditures by eliminating the need for a glycol contactor, and reducing operating expense by having a high chemical recovery factor. It could both inhibit hydrates in the gathering system and could also ensure that the gas separated at the platform would be sufficiently dehydrated to meet the 7-lb/MMSCF pipeline water specification. The glycol facilities on the platform include typical gas/liquid separation and glycol regeneration facilities in addition to the glycol injection pumps. A glycol contactor was not required thus not installed.

Triethylene glycol (TEG) was originally selected as the glycol of choice as it could be easily regenerated to high concentrations at atmospheric pressure. It was also perceived that TEG would be more effective than MEG in dehydrating the gas to 7 lbs/MMSCF at the separator conditions of $60^{o}F$ and 1250 psia. It has been subsequently proven that MEG is equally effective at dehydrating the gas at the same conditions.

To provide hydrate inhibition, the Subsea system was designed to inject glycol at each wellhead. Glycol is pumped from the platform through a common 3-1/2" carbon steel flowline to the subsea manifold, and then via a multitube umbilical from the manifold to each well. Four of the 1" umbilical tubes are dedicated to glycol supply with glycol flow to each well controlled by opening or closing gate valves on the individual flow tubes.

Offshore Operations

Shortly after startup of the first well in July 1997, operating problems appeared in the topsides facilities. Approximately 2 BBL/MMSCF of 37^oAPI condensate were produced although none had been expected. The condensate formed an emulsion with the TEG. Lack of facilities to heat and break the emulsion and separate the condensate resulted in significant amounts of liquid hydrocarbons carrying over into the glycol regeneration system.

Also early in the operations, significant levels of dissolved solids (salts) were detected in the Offshore production stream. Chemical analysis of the glycol indicated well completion fluids to be the source of some of these solids, but the remainder was attributed to salt water production although, again, none had been anticipated.

Continuing ingress of salts and liquid hydrocarbons into the glycol regeneration system led to serious operational problems and repeated fouling and plugging of process equipment including filters, heat exchangers, reboiler, etc. The fouling and plugging could not be controlled even with very frequent changeout of glycol filters. Installation of skimming equipment resulted in improved separation of condensate, but solids continued to be a problem.

The fouling and plugging problems were attributed to a combination of factors. Salt contamination was a major problem. Filtration equipment used at different stages in the regeneration process was inadequate to remove salt from the system since salt crystal growth could not be controlled. The glycol-multicomponent salt solution appeared to supersaturate to the point that the addition of one salt crystal would result in excessive salt deposition. At times a fresh regenerated sample would be collected without any evidence of salt but after sitting on the shelf for 24 hours, significant quantities of salt would precipitate. Certain insoluble glycol degradation byproducts, primarily polyether glycol (PEG), and a wax-like substance also contributed to the plugging problems. After extensive lab experiments and analyses, it was determined that the wax complex was generated from the glycol, magnesium from formation water, high regeneration temperatures and the presence of the base MEA which was used for corrosion control. This wax complex coated the high temperature (350^oF+) solution filters and necessitated filter change-outs approximately every 2 hours.

It became obvious in late 1997 that operation of the regeneration system was not viable and its use was discontinued.   Spent glycol was separated from the production stream on the platform, shipped to shore and stored in tanks. By this time it appeared that contaminated glycol containing unknown concentrations of salts, high cloud point condensate and viscous glycol degradation products had previously passed through the regeneration system and had been pumped into the subsea injection system. This resulted in serious subsea plugging occurrences.

Beginning in late 1997 and continuing until mid-1998, injection pressures in the subsea glycol distribution system varied erratically but generally increased for a given injection rate. This phenomenon was believed to be strongly indicative of system plugging. In some instances glycol flow to one or more umbilical tubes ceased entirely. Analysis of system pressures and pressure drops showed apparent plugging occurring at various times at the manifold, in the umbilical flow tubes and valves and in the main 3-1/2" glycol supply line. Backflow of fluid across the apparent restriction would sometimes eliminate the problem but in many instances this was temporary and the high system pressure drops would recur. At times pressure drop in the injection system increased to the point that operating pressures approached relief valve setting. To maintain operation, glycol injection rates had to be reduced. Lower glycol rates in turn resulted in gas production being curtailed to ensure the proper ratio of glycol to gas for hydrate avoidance.

By early 1998 it became obvious that operation of the existing TEG regeneration system was not feasible. Onshore regeneration was used for a short period to maintain glycol supply, which were leading to transportation and disposal issues and very high operating costs. There existed a critical need to recover, regenerate and re-use glycol and at the same time prevent any additional contaminants from entering the subsea injection system. Also at this point in time the glycol in service was changed out from TEG to MEG due to increased salt solubility capacity, and lower makeup costs.

Glycol Reclaiming Operations

On previous occasions the operator had utilized the services of CCR Technologies Inc. (CCR) to reclaim a contaminated amine-based gas treating solvent at a gas plant near Mobile, Alabama. Based on favorable experience with CCR's patented vacuum reclaiming system, the operator contracted with CCR to reclaim and regenerate the contaminated glycol.

Initially a small CCR reclamation unit was relocated to Abbeville, LA. This unit was able to reclaim a portion of the glycol injection volume required but could not keep up with the system demand so additional make-up glycol was purchased to keep online.

CCR next relocated a larger mobile reclaiming unit to Grand Isle, LA and began processing contaminated MEG on April 1, 1998. It was necessary to ship the contaminated MEG to shore for reclaiming and the reclaimed glycol back to the platform for reuse. The significant statistics for CCR's 19-month Grand Isle operation are:
- Processed 166,001 barrels of contaminated glycol.
- Produced 132,891 barrels of glycol, 31,054 barrels of water and 2,056 barrels of a concentrated liquid residue.
- MEG recovery efficiency 98.6% for the duration of the project and in excess of 99% during 1999.
- Process availability 96%.

The quality of the recovered glycol has been excellent as illustrated by the analysis of the MEG product given in Table 1.

	Incoming Feed	Reclaimed Product
Glycol - wt%	77.4	99.1
Water - wt%	21.0	0.6
Hydrocarbons-vol %	Trace	nd
Suspended Solids - mg/l	68.0	<4
Chloride - mg/l	753.0	nd
Iron - mg/l	18.7	nd
Calcium - mg/l	71.1	nd
Potassium - mg/l	Nd	nd
Magnesium - mg/l	20.0	nd
Sodium - mg/l	175.5	nd

Table 1 Composition of Rich and Lean Glycol for Onshore Reclaiming

Reclaiming MEG in CCR's Grand Isle facility significantly improved operating performance at the offshore facility. This can largely be attributed to the continuous supply of high quality glycol. No field downtime has been attributed to glycol-related issues. Injection system plugging problems have ceased following a mixed solvent flush of the subsea system in August 1998.

CCR Process

CCR Technologies (CCR) is an environmental service company that since 1987 has provided specialized on-site chemical maintenance and reclamation services to the oil and gas and other industries. CCR's proprietary, patented technology is based on vacuum distillation and is capable of purifying virtually any gas treating solvent including MEG. Figure 2 is a simplified block diagram of a CCR process to regenerate and reclaim glycols and amines.
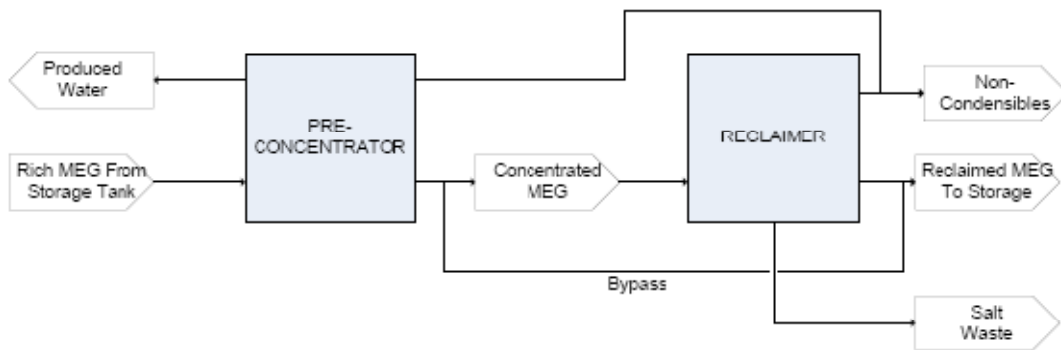
FIGURE 2. CCR Mobile Unit no. 3 Block Flow Diagram

CCR's technology has now been utilized on over 300 projects for more than 70 customers in the natural gas, refining and petrochemical industries. Contamination problems are eliminated in an environmentally safe and cost effective manner. Benefits of the CCR process include:

- Proven for deepwater gas production
- Very high solvent recoveries (i.e. solvent losses minimized)
- Regenerates and reclaims contaminated solvents to produce highly concentrated, high purity product
- Standard equipment and operation (proprietary heating technique designed to reduce fouling potential)
- Waste disposal minimized
- All non-volatile contaminants (solids, salts, degradation products, etc.) removed in one pass
- Solution degradation avoided by low operating temperatures at vacuum conditions
- Virtually no limit on inlet contaminant levels
- Improved process reliability and uptime
- Reduced foaming upsets
- Reduced energy costs
- Reduced filtration costs
- Reduced maintenance costs
- Increased equipment lifetimes
- Corrosion minimized

Offshore Reclaiming Unit

In December 1999 the operator installed a full stream MEG reclaimer (seen in the picture below) on the platform using technology licensed from CCR. This reclaimer has further reduced field operating costs by eliminating the need to ship glycol to shore and back. Conversion of the

hydrate inhibition system from MEG to methanol was considered earlier, but MEG was the more attractive alternative when all factors were considered including capital and operating costs, system uptime and paraffin deposition concerns with methanol.

The design conditions for the offshore reclaimer are outlined in Table 2.

	Current	Future	Design
Gas Rate, MMSCFD	285	190	-
Injected 96 wt% MEG, BPD	450	300	600
Condensed Water, BPD	-	55	110
Formation Water, BPD	-	45	40
Total Water, BPD	100	300	150
Total Unit Feed, BPD	550	600	750
Total dissolved solids, Ton/D	0.13	6.43	1.05

Table 2 Design Parameters of Glycol Regeneration/Reclamation Unit

(Note: TDS is 7000 ppm in the total water for the current case and 15 wt% in the formation water for the future and design cases).

Figure 3 Photograph of Glycol Regeneration/Reclamation Unit

Table 3 outlines the expected and actual operating performance of the glycol recovery unit,

	Expected Performance	Actual Performance
Overall Glycol Recovery Factor	97.1%	99%
Lean MEG concentration	96 to 98wt%	98+ wt%
Impurities in Lean MEG		< 100 mg/l
MEG in water concentration	1000 ppm	< 500 ppm
Availability		96.5%

Table 3 Operating Performance Glycol Regeneration/Reclamation Unit

Although during the first 6 months of offshore operation the unit has met or exceeded process expectations, there have been a few operating problems. The most significant operating problem is related to difficulties in the heat input system. A combination of a heavy hydrocarbon in the feed stream, cross contamination from other sources on the platform as well as equipment problems caused premature fouling of heat exchange equipment and was the largest contributor to the 3.5% downtime. Efforts are being made to reduce the hydrocarbon content in the feed to the GRU, and improve operating procedures, which in turn should reduce the fouling problem. Other contributors to the downtime are more typical startup problems such as seal failures

Conclusion

MEG was the best economic hydrate inhibition solution for this field development. Employing CCR's patented reclaiming technology for salt removal and glycol regeneration solved salt contamination problems. Utilization of this technology has contributed to the success of a major deepwater subsea project in the Gulf of Mexico. Severe operational problems and plugging related to glycol contamination have been eliminated. Implementation of the platform-based reclaimer has further reduced the operating costs. CCR's reclaiming technology provides a cost effective, high recovery, environmentally sound option for subsea developments.

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