**P 068**

# An innovative technique for geochemical analysis of polyol contaminated sediments

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## *Summary*

*KCl-Polymer-Polyol mud system is being increasingly used for reactive shale stabilisation and enhanced drilling performance. Though this mud system improves drilling performance, the polyol contaminated sediments create problem in geochemical analysis as polyol interferes with Programmed Pyrolysis (Rock Eval) peaks of volatile hydrocarbons (S1) as well as of pyrolysable hydrocarbons (S2) and damages the instrument. It is not possible to carry out geochemical pay zone evaluation in the wells where polyol activated mud system has been used as both hydrocarbons and polyol contribute to S1 peak.*

*The present work deals with the study of adverse effect of polyol on geochemical parameters, and their removal from subsurface samples. The sediment samples have been taken from Cambay Basin, India for establishing and testing the methodology. However, the technique is independent of area and applicable to all the basins. A two-step process has been evolved for the removal of polyol prior to geochemical analysis. In the first step, contribution of polyol to S1 peak of Rock Eval has been removed by treating the sediments with ammonium cobaltothiocyanate. The analysis cycle of pyrolyser is customised by truncating the pyrolysis run upto $300^0$C (S1 only) instead of $650^0$C, so that polyol is not introduced in the instrument thereby protecting it from damage by polyol.*

*In the second step, Cobalt complex treated sample is extracted with methanol: acetone: water mixture to remove polyol contribution to S2 peak. Accuracy of S2 peak is further improved by applying numerical correction to bimodal peak.*

*This method is useful for source rock evaluation also as it enables the determination of S1 which helps in determining whether hydrocarbons are in-situ or migratory in nature. It also gives correct value of S2 required for identification of source rock sequence.*

*Thus by introducing successful techniques, problem of identification of hydrocarbon bearing strata and source potential in polyol contaminated samples has been resolved without damaging the equipment and at the same time taking benefit of improved drilling performance provided by use of polyol additive.*

***Keywords:** Polyol, Geochemical analysis, Rock Eval, Ammonium cobaltothiocyanate*

## Introduction

Polyols are established as effective shale inhibitors in water based muds (WBM). Shale inhibition and formation protection is achieved by displacing water from adsorption sites on clay minerals present in shales by polyol and/or by blocking the formation pores from further ingress of invasive fluids by “clouding out” (Reid and Bernadette, 1995).

Polyols enhance lubricity and provide improved overall drilling performance. It is also an ideal system for drilling high-angle wells and horizontal drilling through long pay zone sections where wellbore stability, torque and drag are major concerns (Bloys et al., 1994). It is also used in deep water drilling to depress freezing temperatures and prevent the formation of gas hydrates in the drilling mud (Wenger et al., 2004).

Polyol is a generic name for low molecular weight, water-soluble polymers and oligomers containing a large number of hydroxyl groups. Specific examples include glycols, polyglycols and polyglycerols. Glycols are a series of alcohols with general formula $C_{2n}H_{4n+2}O_{n+1}$. The simplest member is ethylene glycol $C_2H_6O_2$. Polyglycols are polymer or copolymer of an alkalene oxide, such as

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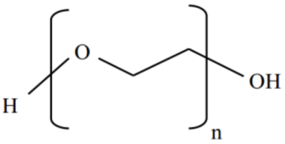
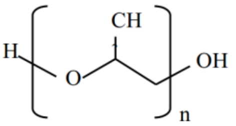
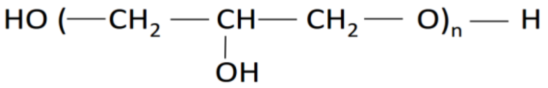
polyethylene glycol (PEG), a polymer of ethylene oxide with general formula HO($CH_2CH_2O$)$_n$H, or polypropylene glycol (PPG), which is a polymer of propylene oxide.





Linear glycerol oligomers have the following structure where n averages 3.



$$HO(-CH_2-\underset{|\atop OH}{CH}-CH_2-O)_n-H$$

## Effect of polyol on Rock Eval

The benefits of polyol additive are obvious, but polyol contaminated sediments create problem in geochemical analysis as it damages the Rock Eval instrument. Flame Ionisation Detector (FID) response drops due to deposit on electrodes, Infrared (IR) detector cell response is also affected. Fine mesh of sample crucible through which hydrocarbons escape out of the crucible gets choked obstructing release of hydrocarbons from crucible and as a result of delayed release of hydrocarbons Tmax value is disturbed. Deposits on pyrolysis and oxidation ovens affect analysis temperature. These deposits cannot be removed by organic solvents. Strong acid is required for their removal which results in corrosion of the parts and ultimately parts need to be replaced. The cost of equipment is about 2 crores.

## Effect of polyol on geochemical analysis

Polyol interferes with both pyrolysis and bitumen analysis. Examples for the study have been taken from Cambay Basin, India. Figure 1 shows increase in S1 and S2 values and decrease in Tmax value after adding polyol to a wellbore sample (Khambel-A, 1270-1285m).

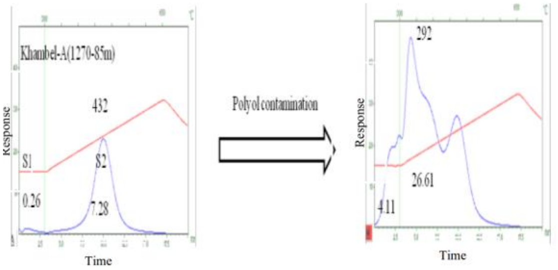
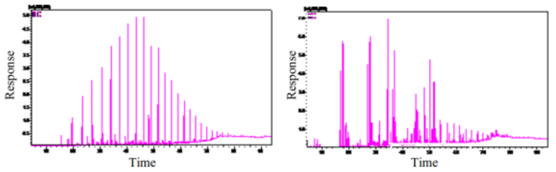


Fig. 1: S1 and S2 peaks of pyrolysis of sediment sample Khambel-A, 1270-85m increase with polyol addition.



Vadatal-A, 2043.5, SWC, No polyol

S Patan-A, 1370m SWC, Polyol

Fig. 2: Effect of polyol on fingerprints of hydrocarbons

Figure 2 shows Total Ion Chromatogram (TIC) of an extract of a side wall core sample taken from well S Patan-A in which polyol was used in the mud system in contrast to that of Vadatal-A in which no polyol was used. Groups of peaks attributed to poly alcoholic compounds are seen in the range where n-alkanes from $C_{10}$ to $C_{27}$ appear thus masking almost the entire range of n-alkane fingerprints. It is difficult to identify hydrocarbons signatures in the extract. Therefore, these contaminants need to be recognised and removed prior to sample analysis.

## Removal of polyol from sediments contaminated by drilling fluid

Bernard et al. (2001) report that satisfactory Rock Eval data can be obtained when polyalkylated glycol contamination is removed using a polar solvent mix of methanol, acetone and water. Wenger et al. (2004) attempted to clean rock samples for source rock analysis using dichloromethane extraction but could not remove all glycol compounds even after multiple extractions.

Singh et al (2007) have reported use of polar mixture of methanol: acetone: water (80:10:10 v/v) for polyol removal. In general 24-36 hours of extraction is recommended. In clay and shale, due to strong bonding, more extraction time of about 48 hours is recommended.

But the use of these organic solvents also removes free hydrocarbons and high molecular weight extractable hydrocarbons and only source rock kerogen is left out in the determined S2 values. Thus valuable information on pay zone and biomarkers which are extensively useful for genetic correlation in source zone is lost.

Geochemical techniques are being used as regular practice for pay zone evaluation, but recently use of polyol mud has increased and this method is no longer applicable in such wells depriving management of such important information for decision making. The purpose of the present work is to remove polyol without affecting the free hydrocarbons.

## Methodology

Ammonium cobaltothiocyanate is being used for determination of nonionic surfactants including polyol (Milwidsky and Gabriel, 1982). Some workers have also used it for determining polyol in mud filtrate (Walker and Henderson, 1997), so we tried to use it for removal of polyol from sediments. Ammonium cobaltothiocyanate reagent was prepared by dissolving 15grams cobalt nitrate hexahydrate and 100 grams of ammonium thiocyanate in distilled water. Temperature was adjusted to ~$20^{0}$C and the solution was diluted to 500 ml in a volumetric flask.10ml ammonium cobaltothiocyanate solution was added to 1g contaminated sediment sample at about $20^{o}$C, while stirring with a glass rod and left it overnight at this temperature. The sample was washed with water till filtrate was colourless. Figure 3 demonstrates that pyrolysis parameters are resorted to original values after treatment with ammonium cobaltothiocyanate and in chromatogram peaks of polyol are removed.

## General procedure for pay zone detection

Figure 4 gives the flow diagram for procedure proposed for pay zone detection. For pay zone studies we mainly use conventional or side wall cores. The sample is taken from the middle to avoid mud contamination. The powdered sample is treated with ammonium cobaltothiocyanate. We observed that it removes contribution of polyol to S1 peak whereas removal from S2 is sometimes only partial. So we propose removal of polyol in two steps-one for S1 and other for S2. The treatment with ammonium cobaltothiocyanate is for S1. But if the analysis cycle is kept usual from 300 to $650^{o}$C, it will harm the instrument by the polyol contributing to S2 peak. Rock Eval has facility of customising analysis cycle, so the cycle was limited for S1 only, i.e. keeping the sample only at $300^{o}$C for 3 minutes. For removal of polyol contribution to S2 peak, the sample is extracted with solvent mixture of methanol, acetone and water as per Bernard et al. (2001) and then analysed in 300-$650^{o}$C cycle. If the shape of S2 peak is still bimodal due to some residual polyol, it can be numerically corrected by taking user defined area of integration.

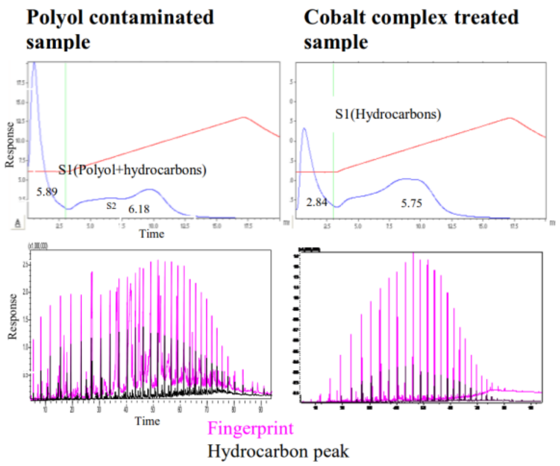


Fig.3: Rock Eval pyrogram and GC-MS fingerprint of sediment sample contaminated with polyol and after treatment with ammonium cobaltothiocyanate shows that the method is effective.

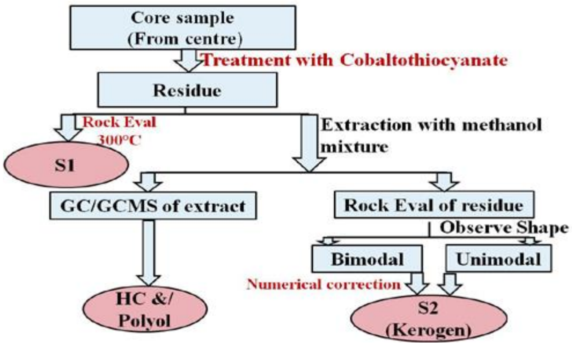


Fig. 4: Flow diagram of procedure for pay zone evaluation

## General procedure for source rock evaluation

For source rock evaluation the number of samples to be analysed per well is about 200-300, therefore it is better to first extract them in one batch with polar solvent mixture for removal of polyol and analyse the extracted samples on Rock Eval (fig. 5). Only samples of interest need to be treated with Co complex to determine S1 due to free hydrocarbons. These selected samples can then be individually extracted for biomarker studies. The extract will have both polyol and hydrocarbons. Due to polarity difference polyol will be retained by silica gel while separating the group types through column chromatography.

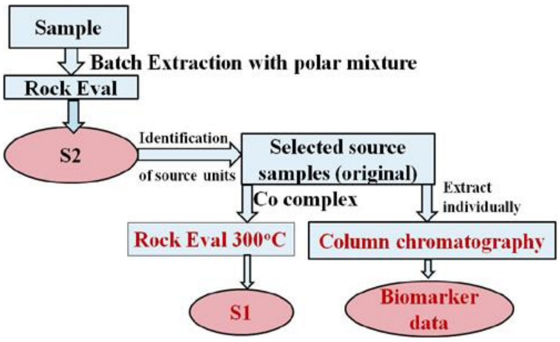


Fig.5: Flow diagram of procedure for source characterization

## Effect of the polyol removal methods on free hydrocarbons and kerogen

Since the objective of this work is pay zone and source evaluation, it is essential that the hydrocarbons are not affected by these methods; therefore samples with known S1 and S2 were used to check the suitability of these methods and it was found that original values are retained after cobalt complex treatment.

## Effect of polyol on conventional cores and side wall cores

Cutting samples are known to be contaminated if polyol is used in mud system and require its removal before any geochemical studies. However in case of conventional cores it was observed that if care is taken to pick the sample from the center of the core no treatment is required whereas side wall cores may or may not be affected by polyol and hence precaution needs to be taken.

## Implementation

With the introduction of this technique of polyol removal, pay zone analysis is being carried out even in wells where polyol is used in the mud system and the results have been confirmed from actual production testing. The technique is general and applicable in any basin. Here case studies have been given from Cambay Basin. In Vadatal-A1, geochemical analysis gave positive indications for oil accumulation in side wall cores at 605, 1622, 1657-1678.5, 2127 and 2131.5m. On testing object II (1654-1663 and 1668-1673m, Chattral) flowed oil @ 22.5m3/d and 6700m3/d gas with 6mm bean. Oil indications (25 litre oil recovered during reverse out) were reported from object I (2112-15 and 2119-27m, Olpad) and object III (1598-1604m, EP IV) gave oil influx 60.42m3 during reverse out (fig.6).

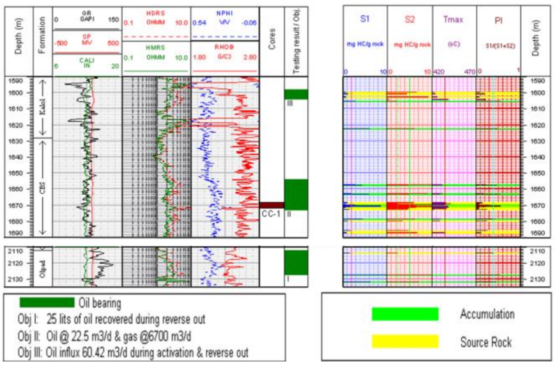


Fig. 6: Geochemical pay zone evaluation in Vadatal-A1

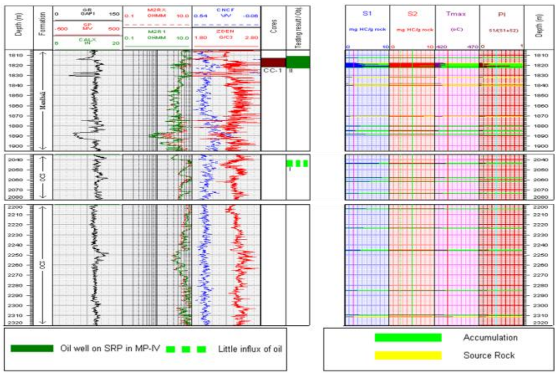


Fig. 7: Geochemical pay zone evaluation in Linch-A

In Uber-A where polyol was used in the mud system, geochemical testing showed absence of migratory hydrocarbons in the core studied. The well was abandoned.

In Linch-A geochemical analysis showed presence of hydrocarbons at 1817-22, 1880-88, 2043.5, 2057.5, 2061.5, 2073, 2223, 2245, 2285 and 2309m after polyol removal (fig. 7). The well is flowing on SRP from 1811-

13, 1819-23m (Mandhali) and influx of viscous oil was observed at 2040.5-47 (OCS). Deeper parts were not tested.

## Conclusions

Treatment of polyol contaminated samples with ammonium cobaltothiocyanate completely removes polyol that contributes to S1 peak of programmed pyrolysis.

Polyol contributing to S2 peak is sometimes not fully removed with ammonium cobaltothiocyanate.

Therefore a two-step process has been evolved for the removal of polyol prior to geochemical analysis. In the first step, contribution of polyol to S1 peak has been removed by treating the sediments with ammonium cobaltothiocyanate. The analysis cycle of pyrolysis is customised by truncating the pyrolysis run upto $300^0$C (S1 only) instead of $650^0$C, so that polyol is not introduced in the instrument thereby protecting it from damage by polyol.

In the second step, Cobalt complex treated sample is extracted with methanol: acetone: water mixture to remove polyol contribution to S2 peak. Accuracy of S2 peak is further improved by applying numerical correction to bimodal peak.

The method is useful for pay zone as well as source rock evaluation.

Thus an innovative solution has been found to a challenging problem of geochemical analysis of sediment samples from wells where polyol mud system has been used.

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