CHEMICAL AND PHYSICAL PROPERTIES

SECTION A12
BIODEGRADABILITY AND BIOCIDAL PROPERTIES

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CABOT

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A12.1 Introduction

An ideal drilling or completion fluid should be biodegradable when discharged to the environment, but should at the same time exhibit biocidal properties when used in drilling and completion applications. In most drilling and completion fluids biocides need to be added to protect fluids and / or additives from biodegradation. Because biocides are intended to kill living organisms, many biocidal products pose significant HSE risk, and the use of such additives should be avoided if at all possible.

Formate brines are unique in that they have biocidal properties at working concentrations, yet they are readily biodegradable when diluted to low concentrations and can be discharged safely to the environment. Their natural biocidal properties at working concentrations means that neither the brines nor the organic additives used in the brines will biodegrade during field application or storage.

For the past ten years, potassium / cesium formate brines have been used without biocides as completion, workover, and suspension fluids in over 150 HPHT well operations. Judging by conventional microbiological tests, these brines seem to have remained sterile and free of viable microorganisms. Potassium / cesium formate brines have also, over the same period of time, been used without biocides as HPHT drilling fluids, again without any apparent problems. Sterility in formate-based drilling muds might be assumed if they are tested conventionally, but the advent of sophisticated FISH (fluorescent in situ hybridization) probes has shown the presence of archaea in several field muds.

A12.2 Biodegradability

The formate ion ($HCOO^-$) is organic, which means that biodegradation testing is required by authorities for discharge of formate fluids. No PARCOM recommended test procedure for biodegradability yet exists, but the most widely accepted test today is a 28-day Ready Biodegradability test, which is carried out in the laboratory under aerobic conditions.

Various aerobic biodegradability studies have been carried out on formate salts by Shell Research [1]. Sodium, potassium, and cesium formate were all tested by 301D (Closed Bottle Test) at Huntingdon Research Centre, England. Results of this study are shown in Table 1. Also, COD, BOD_5, and 301 E (Modified OECD Screening Test) have been carried out on sodium and potassium formate. These studies were conducted for Shell Research at Acer Environmental, and the results are listed in Table 2 and Table 3.

The following definitions are used:

- **ThOD – Theoretical Oxygen Demand**
  ThOD can be calculated from the formula of the substance and its purity, or relative portions of major components.
- **COD – Chemical Oxygen Demand**
  COD is a measure of the 'total' oxygen demand of a substance, and is based on the degree of reduction of an aqueous solution of hot aqueous dichromate.
- **BOD – Biochemical Oxygen Demand**
  BOD is a measure of the oxygen demand of an aqueous solution of a substance when exposed to oxygen in water. The oxygen is consumed by bacteria inoculated into the test cell. The BOD is thus a measure of oxygen demand of a substance in its natural environment. The BOD needs to have a specified period as a substance's oxygen demand increases with time. The normal measurement is taken after five days (BOD_5).
- **BOD / COD**
  The BOD / COD ratio is a measure of the extent of biological degradation.

On the basis of all biodegradability testing undertaken by Shell, it could be concluded that formate brines are readily biodegradable, and they all pass the 'time-window criterion', i.e. substances that achieve 60% biodegradation must do so within ten days of attaining the 10% level.

A12.3 Biocidal properties

One advantage of formate brines over other fluids used for drilling and completion is that they are biodegradable (when diluted) and, therefore, environmentally acceptable. However, when formate brines are used as completion / packer fluids in low concentrations, it is important that the formate concentration is high enough to inhibit bacterial growth.

The formate levels that inhibit bacterial growth have been determined by Shell Research for aerobic and anaerobic bacteria in diluted sodium formate brines [1]. Sodium formate was selected as it is the brine normally used in low-density applications where bacterial growth can be a problem.

Aerobic bacterial growth is largely expected in the surface equipment, and testing was therefore carried out at room temperature. An inoculum that contained a wide range of aerobic bacteria was tested by measuring the removal of dissolved organic carbon (DOC).

Exposure to anaerobic sulphate-reducing bacteria is most likely to occur under down-hole conditions, i.e. at elevated temperature. Therefore, the inhibition test was carried out at temperatures reflecting this. Two cultures of SRB were used, the T670 (mesophilic) that grows optimally at 30°C / 86°F, and the TSRB1 (thermophilic) that grows optimally at 60°C / 140°F. No culture was available that would grow optimally at higher temperatures. As formate is not a 'complete' substrate for SRB, the inhibition tests were carried out in media that supports culture growth in the absence of formate.

With both aerobic and anaerobic bacteria, the inhibition level was found to be approximately 1 M (6.8 %wt), which corresponds to a brine density of about 1.04 g/cm^3 / 8.7 lb/gal. Both tests used 'ideal feeding' conditions, which rarely occur in the field. Tests therefore reflect a worst-case scenario.

Shell testing supports Cabot's field experience, specifically that formate brines are biostatic or biocidal at concentrations normally used for oilfield applications and no addition of biocides is required. There are two unusual instances where bacteria have been found in potassium / cesium formate drilling fluids.

References

[1] Howard, S.K., Houben, R.J.H., Oort, E., Francis, P.A.: 'Formate Drilling and Completion Fluids – Technical Manual', Shell Report SIEP 96-5091, 1996.

Table 1 Ready biodegradability '301 D – Closed Bottle Test'.

Test	Sodium formate (16 mg/L)	Potassium formate (18 mg/L)	Cesium formate monohydrate (45 mg/L)
BOD_{28} [mg O_2/L]	3.85	3.15	3.35
Theoretical Oxygen Demand (ThOD)[1)] [mg O_2/L]	3.76	3.42	4.05
Percentage biodegradation (28 days) [%]	102	92	83
'Time-window criterion'[2)]	Pass	Pass	Pass

1) Calculated as ThOD (sodium benzonate) × conc. (sodium benzonate) + ThOD (formate) × conc. (formate).
2) 'Time-window criterion': substances that achieve 60% biodegradation must do so within ten days of attaining the 10% level.

Table 2 COD and BOD_5 values for sodium and potassium formate.

Test	Sodium formate (16 mg/L)	Potassium formate (18 mg/L)
COD [mg/L = mg/g] (sample 1,000 mg/L)	112	93
BOD_5 [mg/g] (sample 50 mg/L)	4	8

Table 3 Ready biodegradability '301 E Modified OECD Screening Test'.

Test	Sodium formate		Potassium formate	
	11.8 mg/L	31.2 mg/L	11.7 mg/L	30.4 mg/L
Biodegradation (7-day) [%]	13	6	17	6
Biodegradation (14-day) [%]	89	92	92	94
Biodegradation (21-day) [%]	91	94	90	92
Biodegradation (27-day) [%]	81	90	75	89
Biodegradation (28-day) [%]	90	88	80	89