

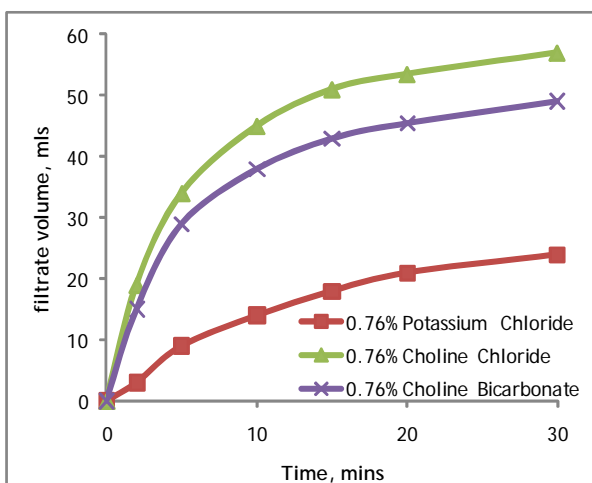
Choline Products: Environmentally Responsible Clay Stabilizers

Clay Stabilization

Drilling and stimulation in shale and other clay containing formations pose challenges due to clay swelling. A number of issues may result from clay swelling, including wellbore instability, cuttings disintegration, bit balling, fines migration and reductions in permeability of the formation to hydrocarbons. These issues can result in higher drilling costs and slower production rates.

Clay stabilizers reduce clay swelling. They function through ion exchange; the clay stabilizer provides a cation to replace the native, easily solubilized sodium. Choline cations as found in choline chloride (75%) and choline bicarbonate (75%) are very effective at preventing the swelling of clay (see Figure 1). They serve as an effective temporary clay stabilizer for the smectite, illite and mixed layer clay minerals, those commonly found in shale formations.

Figure 1. Filtration Time Test



Test Method: 5 grams of API Bentonite and 100 ml of water containing 0.7% swelling inhibitor are mixed in a Waring blender at low speed for 5 minutes. The mixture is passed through a Whatman #2 filter paper. The filtrate volume is recorded as a function of time. For the same level of additive the choline salts show much faster filtration indicating less swelling of the clay.

Choline salts are more environmentally responsible when compared to other clay stabilizers. Key features of choline salts include:

- **Reduced chloride or chloride free:** Chlorides are persistent and do not degrade. The chloride ions pass readily through soil and eventually enter surface water. They then mobilize heavy metals such as cadmium and mercury and can act as a transport helping to deliver these metals to surface or ground water. Most governmental regulations prohibit surface disposal of salt brines containing greater than 3,000 ppm chloride. Choline bicarbonate is completely chloride-free while the use of choline chloride results in reduced chloride levels (when compared to other chloride containing clay stabilizers such as potassium chloride). Choline chloride and choline bicarbonate are liquid, highly effective clay stabilizers. The liquid form eliminates the need to premix salt water prior to the fracturing treatment, eliminating any leftover salt water and the chance of spillage. Furthermore, a high efficiency, low or zero chloride clay stabilizer will lower the chloride levels in flowback water, facilitating potential disposal on location with proper government clearances.
- **Readily Biodegradable:** Choline chloride has been shown to be readily biodegradable according to OECD criteria (93 % biodegradation within 14 days, MITI-I test). The biodegradation was recorded by measuring the biochemical oxygen demand (BOD); a substance is readily biodegradable when 60% biodegradation occurs within 28 days. This result is confirmed by a BOD test performed according to DIN 38409 part 43 (German national biodegradation test) where a 75 % biodegradation was obtained.¹

¹ = Biodegradation data for Choline Chloride found in the Organization for Economic Co-operation and Development (OECD) Screening Information DataSet (SIDS) year 2004.



- **Low toxicity to aquatic organisms:** Balchem has conducted tests to determine the toxicity of choline products to mysids; the results are shown in tables 1 and 2. For drilling fluids to be discharged into the Gulf of Mexico, they must show a mysid 96 hour lethal concentration for 50% mortality (LC50) of more than 30,000 ppm Suspended Particle Phase (SPP). Drilling fluids containing 5% choline salts will easily pass the mysid toxicity test as shown in table 2. For comparison, toxicity data for potassium chloride (KCl) is shown; the choline salts are clearly less toxic to mysids.

Table 1. Mysid Toxicity Tests: Choline Salts	
Swelling Inhibitor	96 Hour LC₅₀ (*), ppm
Choline Chloride	1596
Choline Bicarbonate	1400
Potassium Chloride	560
Test method: 96-hour definitive toxicity test as found in <i>40 CFR 435 Appendix 2 to Subpart A</i> .	

Table 2. Mysid Toxicity Tests: Drilling Fluids Containing Choline Salts	
Swelling Inhibitor in Drilling Fluid	96 Hour LC₅₀ (*), ppm SPP
Choline Chloride	174,000
Choline Bicarbonate	174,000
Potassium Chloride	59,000
Test method: 96-hour definitive toxicity test as found in <i>40 CFR 435 Appendix 2 to Subpart A</i> . Drilling fluids were prepared according to the following formula:	
Component	wt %
Swelling inhibitor	5.0
NaCMC	0.1
Xanthan	0.2
Barite	49.4
Seawater (2.0% NaCl)	45.0
Starch	0.3

(*) LC₅₀ = Lethal Concentration for 50% Mortality

Product Specifications:

Specific gravity = 1.1

pH = 7 – 9 (Choline Chloride),
9 – 11.5 (Choline Bicarbonate)

CAS # 65-48-1; CAS # 78-73-9

Activity = 75 – 78%

Shipping and Handling:

- 500 lbs. in a 55 gallon polyethylene drum
- 1100 kg totes and Bulk

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