

Chemical Oxidation of MTBE and TBA

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ABSTRACT: Methyl tertiary butyl ether (MTBE) is a synthetic chemical that was historically used as an octane booster additive to gasoline. Increasingly there have been concerns about its toxicity and potential carcinogenicity. Because of these concerns, 18 states regulate MTBE levels in groundwater and 17 have banned its use in gasoline. Because of its chemical characteristics, MTBE contaminated sites are difficult to remediate. MTBE readily dissolves and spreads in water. Additionally, MTBE resists biodegradation, does not sorb to soil, and has a low Henry's Law constant. As a result, the extent of MTBE contamination is usually much greater than that of the other common gasoline components. Because of these factors, remediation of MTBE-impacted groundwater can be very difficult and costly.

MTBE can breakdown in groundwater to form tert-butyl alcohol, TBA. TBA is also an impurity in or is formulated with MTBE. Many states are also beginning to regulate TBA in groundwater. The problem of remediating groundwater contaminated with MTBE is complicated by the presence or formation of TBA.

There is a considerable interest in finding an efficient technology that can be used for remediation of MTBE. The utilization of in-situ chemical oxidation (ISCO) is becoming a more common method for treatment of MTBE. Previous case studies and research have shown that a variety of oxidants will reduce concentrations of MTBE. However, the production of tertiary butyl alcohol (TBA) with many of these oxidants poses a significant problem.

Fenton's reagent, permanganate, ozone and uncatalyzed persulfate all produce TBA. The oxidation of MTBE by activated persulfate does not generate much TBA. Additionally, activated persulfate will also oxidize TBA if it is present.

INTRODUCTION. MTBE has been used as a gasoline additive since 1979. It helps fuel to burn cleaner and boosts the octane value. The Clean Air Act requires states with non-attainment for CO (carbon monoxide) to have 2.7% oxygen content in the gasoline used during winter months. This equates to a 15% MTBE content. Federal regulations requiring reformulated gasoline to reduce emissions require a 2% oxygen level (~11% MTBE). It should be noted that the oxygen requirement for gasoline does not specify MTBE; however, MTBE has been the most common oxygenate.

Beginning in the 1990s, there has been increasing public concerns about the effect of MTBE on human health. Much of the public's concern has been driven by the fact that MTBE has a low odor and taste threshold; as low as 5 -20 µg/L with some subjects. The Oxygenated Fuels Association in 1998 recommended a secondary contaminant level for taste and odor of 15 µg/L as being protective of 95% of the population. There is little human health data for MTBE. However, in some animal studies, drinking water with MTBE caused gastrointestinal irritation, liver and kidney damage, and nervous system effects in rats and mice. Inhalation of MTBE for long periods in one study with rats caused kidney cancer; another study with mice resulted in liver cancer (ASTDR 1997).

This public concern has led to increasing regulatory scrutiny on MTBE use and its presence in groundwater.

Currently 18 states regulate MTBE in groundwater with clean-up levels ranging from 5 to 240 µg/L. A total of 17 states have enacted legislation either banning the use of MTBE outright or restricting its concentration in gasoline and part of the year it can be used.

The concern with MTBE has been extended to other oxygenates. Oxygenates approved by the U.S. EPA include methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), and diisopropyl ether (DIPE), ethanol (EtOH),

State	MTBE	TBA
California	5-13	12
Maryland	10	25
New York	50	50
New Jersey	70	100
Massachusetts	70	120
Missouri	40	104
Florida	50	1,500
Wyoming	200	3,200
Michigan	240	3,900

tert-butyl alcohol (TBA), and methanol (MeOH). TBA is unique among these oxygenates in that it can be formed by the degradation of MTBE, and is, in fact, a common co-contaminant at MTBE sites. Approximately 360 of 500 MTBE sites had significant levels of TBA (Koltahar 2003). As a result and as shown in Table 1, a number of states

are now also regulating TBA levels in groundwater. In general, the regulatory standards for TBA are higher than the equivalent standards for MTBE. Given these clean-up levels, processes that treat MTBE have also to address TBA.

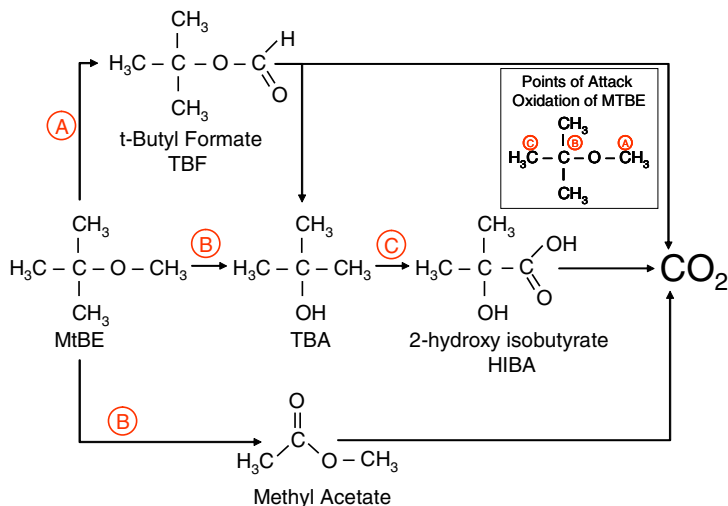
Treating both MTBE and TBA is not easy as they have different chemical and physical properties as summarized in Table 2. TBA is much more soluble than MTBE. It is less volatile. Therefore it will not respond as well as MTBE to SVE/air sparging or to pump and treat. TBA and MTBE have opposite biological responses. Neither is readily biodegradable. MTBE degrades easier under anaerobic conditions (usually to TBA). TBA degrades aerobically. Thus TBA tends to increase in the downgradient direction relative to MTBE until the plume becomes aerobic.

Property	MTBE	TBA
Solubility (mg/l)	43,000	Miscible
Henry's Constant	0.022	0.00053
Log K _{oc} (Sorption)	1.0 – 1.1	1.5 – 1.8
Vapor Pressure, mm Hg	245	40 – 42
Aerobic Biodegradability	Poor	Fair
Anaerobic Biodegradability	Fair	Poor

In-situ chemical oxidation (ISCO) has been a rapidly developing remediation tool for treating groundwater contamination. There are currently four oxidant systems being employed: hydrogen peroxide, potassium/sodium permanganate, sodium persulfate, and ozone. Hydrogen peroxide has several variations including “Classical Fenton’s Reagent” (acidic, inorganic ferrous iron); “Modified Fenton’s Reagent” (chelated ferrous/ferric iron, neutral pH); and peroxide adducts such as calcium peroxide and sodium carbonate peroxide, which hydrolyze to release hydrogen peroxide. Ozone is a unique oxidant system since it is a gas. The other oxidant systems are aqueous based.

There has been renewed interest in using ISCO to treat gasoline sites, in part, because it appears that MTBE may be readily oxidized. However, given the concern with TBA an important question is: What is the effect of these oxidants on the presence or the formation of TBA. Is TBA produced and does it persist?

Figure 1: Potential MTBE Oxidation Pathways



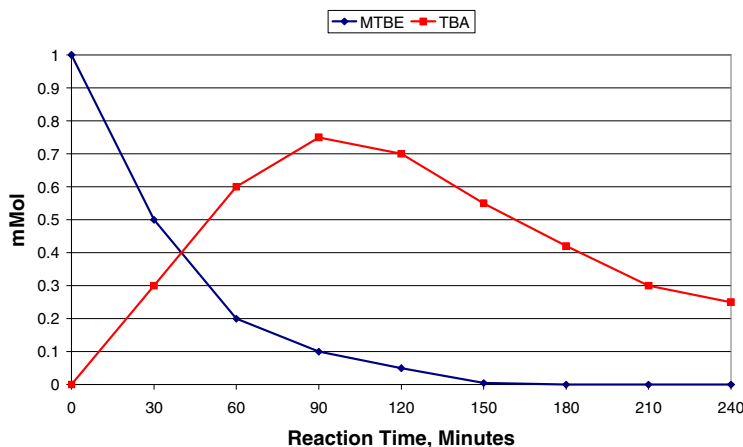
OXIDATION RESULTS

When MTBE is oxidized, the oxidant generally attacks a carbon atom. As shown in Figure 1, there are three “types” of carbon atoms – the methyl group attached to the oxygen (A), the tertiary carbon (B), and the methyl group attached to the tertiary carbon (C). Figure 1 also shows some of the potential pathways and products that can be formed

during oxidation. Attack at (A) leads to the formation of ter-butyl formate (TBF). Attack at B can lead to TBA or methyl acetate. Based on a review of the literature and on the products reported, it does not appear that the initial oxidant attack is at (C). However, if TBA is formed, attack at (C) forms 2-hydroxy isobutyrate (HIBA).

Each of the four oxidants was tested with MTBE. TBA and MTBE levels were tracked to see if TBA accumulated. Persulfate and permanganate were also tested with a mixture of TBA and MTBE. The results are depicted in the following figures.

Figure 2: Oxidation of MTBE with Ozone



Ozone:

Figure 2 shows the results for the oxidation of MTBE with 10% ozone (in oxygen). Ozone rapidly oxidizes MTBE. However, TBA is formed in near stoichiometric quantity. TBA is also oxidized but at a slower rate than is MTBE. Given the near stoichiometric conversion of MTBE to TBA it would appear that ozone attacks the

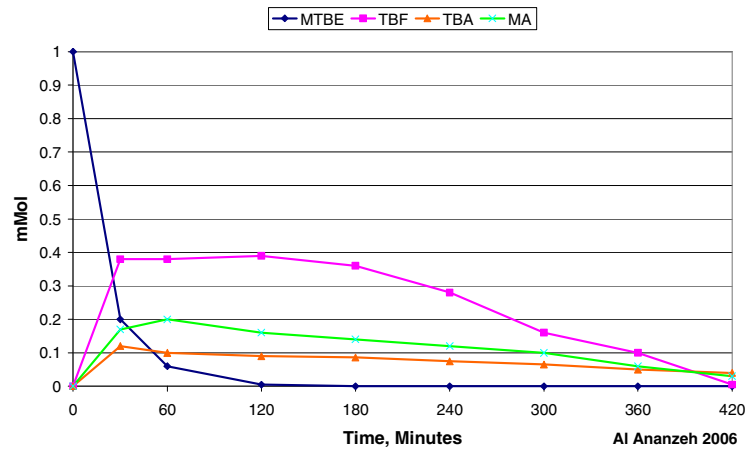
tertiary carbon (B). The reaction displaces the methyl-oxygen forming methanol.

Hydrogen Peroxide:

Figure 3 shows the oxidation of MTBE with 500 mg/L H_2O_2 and 100 mg/L Fe^{+2} at a pH of 2.8 (Al Ananzeh 2006). The reaction was analyzed for multiple products. The primary

products (formed directly from MTBE) were, in decreasing order, TBF, methyl acetate (MA), and TBA. Acetone was also formed and was a secondary oxidation product derived from one of the primary products. Only about 10% of the MTBE was converted to TBA. All of the primary products also degrade. However the rate of degradation for TBA is the slowest. TBF degrades five times faster than TBA; MA, three times. Based on the products formed it appears that both the (A) and (B) carbons were attacked.

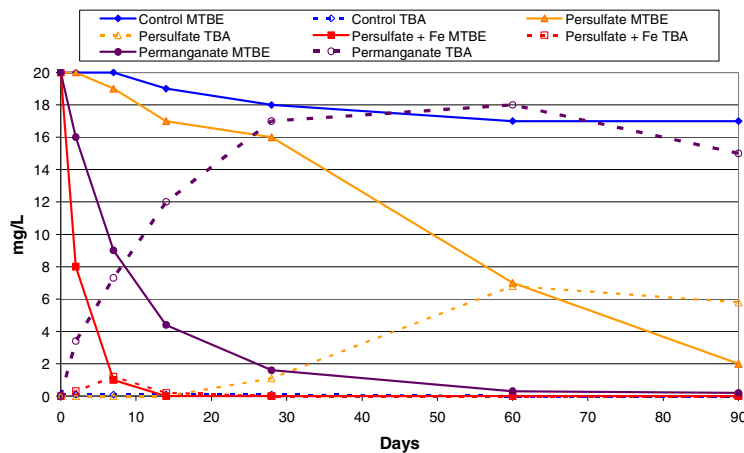
Figure 3: Oxidation of MTBE with Fenton's



Persulfate and Permanganate

Figure 4 depicts the results for the oxidation of MTBE with 5% potassium permanganate at a pH of 6 – 7; 10% sodium persulfate at an initial pH of 6 – 7; and, 10% sodium persulfate with 250 mg/L of ferrous iron at an initial pH of 6 – 7. Only TBA was analyzed as a reaction product. As can be seen from the figure, permanganate oxidizes MTBE but the oxidation reaction results in a stoichiometric conversion to TBA on a molar basis. The TBA appears to be quite stable and only slowly degrades in the presence of permanganate. There is only a 10-12% decrease in TBA levels over a 60 day period after the MTBE is essentially gone (30 to 90 days).

Figure 4: Oxidation of MTBE with Persulfate & Permanganate



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Two persulfate systems were examined. One was unactivated; the other used iron II activation. Persulfate activation,

which is compound specific, is often a key factor in the use of persulfate (Brown 2006).

The results for the two persulfate systems were quite different. Unactivated persulfate did slowly oxidize MTBE. After 90 days of treatment there was still 10% of the MTBE present. The oxidation reaction did produce TBA as a byproduct. The TBA level produced was, at a maximum, about 42% of the original MTBE present on a molar basis. The TBA was also oxidized but at a much slower rate than did the MTBE. By contrast, the iron activated persulfate resulted in a rapid oxidation of MTBE, with very little

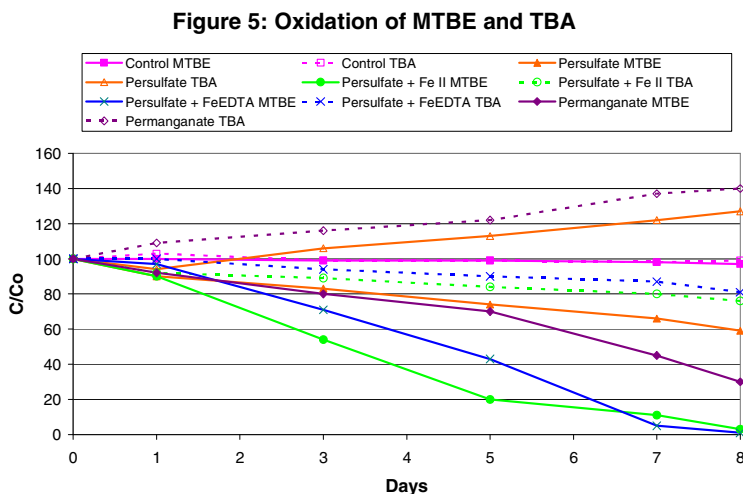
production of TBA. The TBA was, at a maximum, less than 10% of the original MTBE level on a molar basis. It was also rapidly oxidized by the iron-activated persulfate and was not present after 14 days.

Based on these results, it would appear that unactivated persulfate oxidation results in attack at the (B) carbon. It may also form TBF; however, TBF was not analyzed. Activated persulfate appears to proceed by a different pathway, as little TBA is formed and does not persist.

Other studies examined other activation systems for persulfate such as heat activation or activation by high pH. Both of these systems oxidized MTBE without any accumulation of TBA.

Oxidation of TBA and MTBE

As a follow up to the study of MTBE oxidation, the effect of several oxidants on the oxidation of mixtures of MTBE and TBA were also examined. Permanganate and



persulfate were tested. Three persulfate systems were tested – unactivated persulfate, persulfate activated by iron II sulfate, and persulfate activated by iron III EDTA complex. A 10% persulfate was used and the iron level was set at 250 mg/L as Fe. None of the systems were pH adjusted. All started out at a pH of 6 – 7. The pH of the persulfate systems became acidic over time. The permanganate study used a 5% potassium permanganate. The results are depicted in Figure 5. The results are expressed as C/C_0 as a function of time. Equimolar quantities of TBA and MTBE were added initially. An increase in the C/C_0 for TBA means that it was produced by the oxidation of MTBE at a rate that was less than any oxidation rate resulting in a net increase. A decrease in the C/C_0 for TBA means that it was oxidized at a rate greater than the rate of conversion of MTBE to TBA (if it does occur.) Two of the oxidant systems resulted in a net increase in TBA over time – permanganate and the unactivated persulfate. Both slowly oxidize MTBE producing TBA. The permanganate results in a greater conversion of MTBE to TBA. Neither oxidant system shows any substantial reduction in TBA levels over the course of the experiment.

Both of the activated persulfate systems show rapid and complete oxidation of MTBE over the course of the study. Both also show a slower oxidation of TBA. Based on the previous study (Figure 4) one can project that little, if any, TBA was formed by the oxidation of MTBE. The rate of TBA oxidation is about 1/5th the rate of MTBE oxidation.

As a follow up to the study of MTBE oxidation, the effect of several oxidants on the oxidation of mixtures of MTBE and TBA were also examined. Permanganate and persulfate were tested. Three persulfate systems were tested – unactivated persulfate, persulfate activated by iron II sulfate, and persulfate activated by iron III EDTA complex. A 10% persulfate was used and the iron level was set at 250 mg/L as Fe. None of the systems were pH adjusted. All started out at a pH of 6 – 7. The pH of the persulfate systems became acidic over time. The permanganate

DISCUSSION. ISCO is an effective means of treating MTBE contamination. All four of the common oxidant systems – hydrogen peroxide, permanganate, persulfate and ozone, were able to effectively oxidize MTBE. The rates of oxidation of MTBE vary. The fastest appear to be hydrogen peroxide (Fenton's Reagent) and ozone. The slowest are permanganate and unactivated persulfate. Persulfate activated with inorganic or chelated iron had an intermediate reaction rate.

The oxidant systems varied in the production of TBA during the oxidation of MTBE. Permanganate oxidation of MTBE resulted in essentially stoichiometric production of TBA. Ozone also showed a high degree of conversion of MTBE to TBA. Unactivated persulfate resulted in appreciable TBA production but TBA was not the major reaction product for either of these oxidant systems. Unactivated persulfate converted about 40% of the MTBE to TBA. The Fenton's reaction did produce TBA, resulting in a 10% conversion of the MTBE to TBA. However, TBF and methyl acetate were the main products formed by the Fenton's oxidation of MTBE. Activated persulfate produced very little TBA, less than 10% of the MTBE.

The reaction of TBA with the oxidants was highly varied. Only the activated persulfate systems and ozone showed any appreciable oxidation of TBA, but at rates several times slower than the rate of MTBE oxidation. Unactivated persulfate showed a slow oxidation of TBA. Permanganate showed very little oxidation of TBA. Based on these results it would appear that TBA would accumulate when using peroxide, permanganate and unactivated persulfate. Ozonation would have to continue for a period of time after MTBE is oxidized to fully oxidize the TBA. Only the use of activated persulfate assures that TBA residuals are not an issue.

On sites where TBA is already present, the proper choice of an oxidant system is even more critical. Activated persulfate would give the best results, simultaneously destroying both MTBE and TBA. Ozone would also be effective but would have to be continued for a period of time after the MTBE is destroyed. Peroxide and permanganate would not be effective in treating any TBA already present.

CONCLUSION. ISCO is potentially an effective tool for treating sites with MTBE contamination. However there is a substantial difference in performance among the different oxidant systems. The studies discussed above examined the rate of MTBE oxidation, the production of TBA and the rate of TBA oxidation. These factors can be used to rank the different oxidant systems.

In ranking the different oxidant systems, other factors should also be considered. Most MTBE contamination is associated with gasoline spills. As a result there is also BTEX contamination. Therefore, another ranking factor is the treatment of BTEX and also total petroleum hydrocarbons (TPH) associated with gasoline. Many gasoline sites also have associated soil contamination. ISCO can be used to treat soil contamination, but it generally necessitates that the oxidant either rapidly reacts with the adsorbed contaminants or persists in the subsurface long enough to continue to react as the soils contaminants desorb into groundwater. The safety and handling of the different oxidants varies, especially on gasoline sites. Finally, many sites transition into MNA as the final remedy stage. Compatibility with MNA, primarily biological systems is also a consideration.

Table 3 summarizes these different factors and provides a ranking of the different oxidant systems for treating MTBE contaminated sites. The ranking is the order in which the oxidants are listed. As can be seen from the table, activated persulfate is by far the best suited system for treating MTBE sites.

The application of ISCO has two variants. Ozone is a gas and therefore requires essentially an AS/SVE system to distribute the ozone and to collect any residual ozone and any VOCs that are liberated. The remaining oxidants are all aqueous based. There are a number of injection systems that can be used for the different oxidants. One can use injection wells and galleries or one can use direct push injections. The spacing of the injection points varies considerably and is a function primarily of the half-life of the oxidant in soil. Hydrogen peroxide has the shortest half-life and therefore requires the closest injection spacing. With peroxide there is little migration beyond the radius of injection. Permanganate and persulfate have a long enough half-life that one can rely on groundwater transport to help in the distribution.

Peroxide has some unique safety issues. Peroxide decomposition is generally catalyzed by iron and manganese minerals. When peroxide decomposes it generates heat and oxygen. At concentrations above 11%, hydrogen peroxide decomposition will reach the boiling point of water also generating steam. This results in considerable gas production. For example, decomposition of a 30% hydrogen peroxide solution will result in a 600-fold volume expansion within a short period of time. The increase in oxygen content and temperature increase the risk for fire, especially if there is separate phase gasoline present.

Given its reactivity with both MTBE and TBA, its improved stability, and improved safety and handling, activated persulfate is the best choice for treating gasoline sites where MTBE is an issue. Activated persulfate provides a rapid, effective and inexpensive remedial method for gasoline sites.

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Table 3: Applicability of Oxidant Systems to the Treatment to MTBE at Gasoline Sites
Order Reflects Applicability/Utility

Oxidant	Oxidation Of MTBE	Production of TBA	Oxidation of TBA	Oxidation of BTEX	Oxidation of TPH	Stability & Reactivity in Soil	Safety & Handling Issues	Compatibility with MNA
Activated Persulfate	Fast and complete	Virtually none produced	Moderate rate of oxidation. Will oxidize mixture at same rate as MTBE alone	Oxidizes all BTEX at same rate as MTBE	Will oxidize TPH but rate is slow.	Half life in soil is 20-40 days. No reaction with soil organics	Strong oxidizer but no special requirements	Compatible with MNA. Stimulates sulfate reduction
Ozone	Fast and complete	>80% conversion to TBA	Will also oxidize TBA but much slower rate than MTBE. Transient accumulation of TBA No persistence.	Oxidizes all BTEX at same rate as MTBE	Will oxidize TPH at moderate rate. TPH oxidation rate comparable to TBA	Reacts directly with adsorbed contaminants. Treats soil	Need to collect unreacted ozone. Requires SVE system	Will depress biological activity. Aerobic bacteria will rebound after ozonation stopped.
Unactivated Persulfate	Slow oxidation	>40% conversion to TBA	Very slow oxidation of TBA. TBA will accumulate and persist.	Oxidizes all BTEX at same rate as MTBE	Will oxidize TPH but rate is slow.	Half life in soil is 20-40 days. No reaction with soil organics	Strong oxidizer but no special requirements	Compatible with MNA. Stimulates sulfate reduction
Peroxide (Fenton's)	Fast and complete	~10% conversion to TBA	Very slow oxidation of TBA. TBA will accumulate and persist.	Oxidizes all BTEX at same rate as MTBE	Will oxidize TPH but rate is slow.	Very short half life in soil - < 1 day. Poor treatment of soils.	Decomposition results in oxygen and heat. Can cause fires if NAPL present	Will depress biological activity. Aerobic bacteria will rebound. Provides residual oxygen
Permanganate	Moderate Rate, complete oxidation	100% conversion to TBA	Very slow oxidation of TBA. TBA will accumulate and persist.	Does not oxidize benzene. Oxidizes TEX	Will oxidize TPH but rate is slow.	Very persistent in soil. But will react with natural soil organics	Strong oxidizer but no special requirements	MnO ₂ Residual dominates bacterial activity. Impedes MNA in treatment area. Downgradient is fine.