

Possible reactions induced by persulfate during hydraulic fracturing

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Persulfate is one of the potential additives applied in hydraulic fracturing acting as a gel breaker to facilitate proppant migration into the created fractures. Even at slightly elevated temperatures ($\geq 40^\circ\text{C}$) the peroxide bond in persulfate can cleave yielding highly reactive sulfate radicals ($\text{SO}_4^{\bullet-}$) (Waldemer et al. 2007). Besides thermolysis, chemical reduction of persulfate in its reaction with low valent transition metals also yields $\text{SO}_4^{\bullet-}$ (Anipsitakis and Dionysiou 2004). Both pathways are principally possible during hydraulic fracturing yielding free radicals. $\text{SO}_4^{\bullet-}$ is a strong oxidant displaying a fast reaction kinetics towards a large variety of organic and inorganic compounds (Neta et al. 1988) and can initiate a large number of reactions during the hydraulic fracturing event. On the one hand this reaction contributes to the desired reaction (gel breaking) on the other hand it also may induce undesired reactions yielding harmful oxidation by-products. The reaction system initiated by $\text{SO}_4^{\bullet-}$ is very complex and it is hardly predictable what kind of products can be formed. This is aggravated by the formation of secondary reactive species. One source of secondary reactive species is the reaction of $\text{SO}_4^{\bullet-}$ with chloride. At low pH (e.g., $< \text{pH } 4$) this reaction yields various radicals with different oxidation states of chlorine (e.g., Cl^\bullet , $\text{Cl}_2^{\bullet-}$, ClO^\bullet) whereby chlorate may represent a stable final product (Lutze et al. 2015). The reactive chlorine species could form harmful chlorinated organic compounds in presence of organic matter. With increasing pH-value hydroxyl radicals are formed in the reaction of $\text{SO}_4^{\bullet-}$ plus chloride representing an additional reactive species (McElroy 1990). Analogous reactions may happen to appear in presence of bromide and iodide leading to bromate, iodate or respective halogenated organic compounds (for further information on reactions of bromide see (Fang and Shang 2012, Heeb et al. 2014, Lutze et al. 2014, von Gunten and Oliveras 1998))

The formation of harmful by-products during the hydraulic fracturing process, have to be included in risk assessment and are mandatory to design a suitable treatment of the wastewater produced during fracking. This demands detailed knowledge on the chemical reactions at conditions of hydraulic fracturing which is largely lacking. First indications of possible reactions initiated by persulfate are presented in the present work.

Literature

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