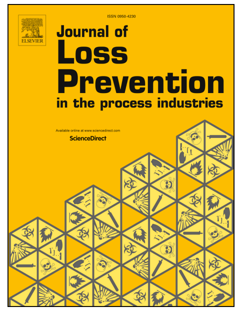

Kinetic analysis for spontaneous combustion of sulfurized rust in oil tanks

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Kinetic analysis for spontaneous combustion of sulfurized rust in oil tanks

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ABSTRACT: In order to evaluate the spontaneous combustion hazards of sulfurized rust in oil tanks, one kind of rust was obtained from respiratory valve inner cavity of a crude oil tank in a petrochemical company. The rust was sulfurized in sulfuration experimental apparatus. The production was analyzed by X-ray energy dispersive spectrometry (EDS), scanning electron microscopy (SEM) and then thermo-gravimetric analysis (TGA). The EDS result shows that the main substances are FeS and FeS_2 which are liable to spontaneous combustion. The sulfurized rust gives a short length of side and diamond appearance, and a large pore size in structure based on X-ray Diffraction (XRD). The whole oxidation process has three complex stages. The corresponding apparent activation energy values, most probable mechanism functions and pre-exponential factor values were calculated by Madhusudanan-Krishnan-Ninan method and the master plot method. The results indicate that the first and third stages of mass loss are up to the power function mechanism, but the second stage accords with the nucleation and nucleus growth mechanism. The values of apparent activation energy increase successively from the first stage to the third stage. The second stage has the maximum pre-exponential factor value, while the first has the minimum. With the obtained parameters above, the oxidation process of sulfurised rust could be simulated, which would benefit for monitoring and early warning of oil tanks.

Keywords: Oil tank; Sulfurized rust; Spontaneous combustion; Most probable mechanism function; Apparent activation energy; Pre-exponential factor

1 Introduction

Rust formed on the inside-walls and respiratory/safety valve inner cavity of crude oil, gasoline or diesel tanks reacts with hydrogen sulfide at low-temperature, which results in formation of sulfurized rust. The major components of iron sulfurized rust are iron sulfide. Some kinds of iron sulfides cause violent exothermic oxidizing reaction and lead to accidental explosion or fire when they are exposed to the air. In Sinopec Group or China National Petroleum Corporation (CNPC), spontaneous combustion of sulfurized rust in oil tanks occurs regularly (Zhao, Jiang, & Zheng, 2011; Zhao, Wand, Li, Ding, & Wan, 2007). Therefore, it is important to know the spontaneous combustion mechanism of sulfurized rust.

Based on all available literature, reports on dealing with kinetic analysis for spontaneous combustion of sulfurized rust were scarce. However, the oxidation of sulfurized rust has been studied in details (Li, Wang, Zhang, & ZHAO, 2011; Li, Li, & Zhao, 2006; Li, Li, & Zhao, 2005; Walker, Steele, & Morgan, 1997; Walker, Steele, & Morgan, 1996) along with variable ambient temperature, hydrogen sulfide concentration, and operation condition of oil tanks. Considering the heat properties of sulfurized rust, evaluation of spontaneous combustion hazards requires experimental methods. These experimental methods can be described as self-heating methods and temperature-programmed experiments (Malow, & Krause, 2004). The self-heating methods (Chen, 1999; Jones, Chiz, Kou, & Matthew, 1996) include adiabatic experiments, the standard wire mesh basket test and the appropriate Frank-Kamenetskii (F-K) analysis, as well as the crossing-point temperature (CPT) method. The

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