

Comparison of polycyclic aromatic hydrocarbons emission from thermal treatment of petroleum sludge cake in the presence of different additives

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This study evaluates effectiveness of 4 additives [CaO, Ca(OH)₂ + NaHCO₃, H₂O₂, and FeSO₄ + H₂O₂] in thermal degradation of hazardous polycyclic aromatic hydrocarbons (PAHs) in petroleum sludge cake. Residual concentrations of 16 priority PAHs were determined using GC-MS. Total PAH conc. was found as: gas, 3.11×10^{-4} - 4.36×10^{-4} ppmv; particulate, 7.92×10^{-5} - 5.24×10^{-4} mg/m³; and residue, 1.37×10^{-4} - 1.07×10^0 µg/g. Total toxicity equivalence of PAHs relative to that of benzo[a]pyrene (BaP) was found as: gas, 3.11×10^{-7} - 4.41×10^{-7} ; particulate, 3.87×10^{-7} - 3.85×10^{-5} ; and residue, 6.17×10^{-7} - 9.65×10^3 . Ca(OH)₂ + NaHCO₃ was most suitable due to least emission of high molecular weight PAHs, lower equivalent carcinogenicity of products, and lower concentrations of PAHs in gas, particulate and residue.

Keywords: Additives, Petroleum sludge cake, Polycyclic aromatic hydrocarbons (PAHs), Thermal treatment

Introduction

Petroleum sludge (world production, 230,000 million tons per annum) contains¹: hydrocarbons, 10-30; solids, 5-20; and water, 50-85%. A major cause of hazardous characteristics of sludge is the presence of polycyclic aromatic hydrocarbons (PAHs). United States Environment Protection Agency (USEPA) has identified 16 PAHs as priority compounds^{1,2} (Table 1). Toxicity equivalence factor (TEF) of PAHs reflects their relative carcinogenic potential as a quantitative cancer risk with reference to benzo[a]pyrene (BaP)^{3,4}. Liu *et al*⁵ found lung cancer risk among foundry workers higher due to gaseous phase PAH exposure than particulate phase. Rojas *et al*⁶ calculated total toxicity equivalent concentration (TEC) from TEF to compare toxicity of particulate emission and found no significant difference in TEC from diesel and palm oil based biodiesel (B15). Biological treatment (bioremediation & phytoremediation) is not commonly used to degrade PAHs due to low yield, long treatment duration and process performance

unpredictability¹. Among chemical treatment (permanganate oxidation), Brown *et al*⁷ reported that BaP, Pyr (pyrene), Phe (phenanthrene), and Ant (anthracene) were reduced 54-72% in 30 min using 160 mM KMnO₄, whereas Flu (fluorene) and Chr (chrysene) were reduced 8-13%. Ball-milling technique showed good degradation for low molecular weight (LMW, 2-3 rings) PAHs, but has no information on high molecular weight (HMW, ≥ 4 rings) PAHs degradation⁸. ElectroChemical GeoOxidation (ECGO) treatment for eliminating PAHs from solidified crude oil showed that priority PAHs were not detectable after 74-124 day test period⁹. Dadhkah & Akgerman¹⁰ employed sub-critical water and hydrogen peroxide (H₂O₂) to degrade PAHs in soil to undetectable level. Nam *et al*¹¹ observed enhanced biodegradation of PAHs in former manufactured gas plant soils; combination of biodegradation with a modified Fenton reaction yielded 85% degradation of 4 and 5-ring PAHs. Kiln incineration³ (820-1600°C) completely degrades all priority PAHs. High operating temperature requires significant energy input that translates into high treatment cost; \$475-1350 per cubic yard¹² (or \$328-843 per m³)¹³. Chou *et al*¹⁴ conducted thermal treatment of synthetic PAH-

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