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# Potential Use of Polyacrylamide Encapsulation for Treatment of Petroleum Drilling Cuttings and Hydrocarbon Contaminated Soil

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**Abstract**

Mineral soil of alluvial origin, contaminated with diesel+lubricating oil (1:2), was treated with a commercial polyacrylamide product at 100% of the distributer recommended dosage, producing a reduction in hydrocarbon concentration (EPA 9074) of 76% that remained stable during the study period (38 days) and even after thermal treatment (60ºC, 18 hrs.). Increasing the dosage to 150% did not improve the treatment results, but repeating the treatment (at 100%) resulted in a slight additional reduction (4%). Similar results were obtained with oil-based drilling cuttings (~60% reduction at both 100% and 150%). Pre-drying of the drilling cuttings prior to treatment did not improve the hydrocarbon reduction, but it did produce smaller, potentially more stable aggregates (0.5–1-0 mm in diameter). The treatment of organic soil resulted in a similar reduction in hydrocarbon concentration (65%) and a reduction of acute toxicity (Microtox) to below background levels, however this effect was not stable. An additional application (including mixing) of the polyacrylamide product resulted in partial disintegration of the organic fibres and release of the stabilized hydrocarbons, measuring an overall increase in hydrocarbon concentration of 19%.

***Keywords:*** stabilization; remediation; waste treatment; soil; petroleum

## 1. Introduction

The increased need in the globalized economy for energy and petrochemical feed stocks has led to a very heavy pressure to produce petroleum and gas. The south and south-east Asia regions have been no exception. The ASEAN countries plus China and India produce almost 10% of the world total for petroleum (EIA, 2010). During the perforation of oil and gas wells, drilling cuttings are produced which require adequate treatment to avoid environmental consequences. Also, improper maintenance of pipelines, as well as clandestine bunkering, lead to uncontrolled spills, contaminating the surrounding soil. This generates is a need for effective and simple alternatives to treat these contaminated materials.

One of the most used methods to treat contaminated soils, sludges and cuttings has been by bioremediation, due to the low cost involved (Adams *et al*., 1999). The main disadvantage of biological treatment technologies is the relatively long time (and thus also space) required. Other methods have also been developed for more rapid treatment including co-processing in cement ovens, re-use as road base or for bricks, micro-encapsulation using silicate or carbonate based materials, and thermal desorption (Adams and Rangel, 1999; Domínguez, 2008; Garcilazo, 2001; Sevilla, 2001; Shah *et al*., 2003; Alvarez, 2010). In the effort to have more treatment options, including relatively fast and simple methods, we investigated the use of polyacrylamide encapsulation.

Polyacrylamide has been used as a flocculant to treat waste waters contaminated with organic particulates for several decades (Wong *et al*., 2006). The advantage in using this flocculant is that it is very effective, of moderate cost, and relatively easy to use. Furthermore, it is of very low toxicity and relatively stable (Kay *et al*., 1998; Ver Vers, 1999). Due to its polymerizing properties and low toxicity it has also been used as a soil stabilizer to reduce soil erosion (Wallace and Wallace, 1989; WisDOT, 2001). It's potential use for treatment of drilling cuttings and contaminated soil was investigated in this study.

## 2. Materials and Methods

The polyacrylamide product (Floculante Mardupol C.H.A., a proprietary formulation) was obtained from Productos Químicos Mardupol S.A. de C.V. in Mexico City.

Slightly contaminated surface soil (0-25 cm) of alluvial origin was collected using a hand shovel near well No. 35 in the Samaria oil field (Tabasco, Mexico). To increase the oil concentration, a mix of 1:2 weathered diesel fuel and spent automotive lubricating oil (SAE 40W) was prepared and hand sprayed on the soil, which had been placed in an aluminium tray. The hydrocarbons were mixed into the soil by hand until it was completely homogenized. The soil was let to stabilize for 18 hours. A portion of the soil was saved to determine the initial hydrocarbon concentration. Subsequently, the polyacrylamide product was added in a proportion equivalent to 2.5 L of concentrated product per cubic meter of soil, which was recommended as a 100% dose by the distributer. This dosage was added by diluting 1:80 in de-ionized water so that the final solution added would be sufficient to produce a moisture content in the soil of approximately 50-75% of field capacity (so that the polyacrylamide-soil mixture was neither too muddy nor too dry). The product solution and the soil were thoroughly homogenized and let to set at ambient temperature (~28ºC) to stabilize the chemical reaction. Samples were collected initially (without treatment) and at 2, 16 and 38 days, to test the durability of the stabilization. This same process was repeated at a 150% dosage of the product. Moreover, an additional application was made at each dosage to determine if any further stabilization could be achieved. To determine the stability to heat (such as that which might be experienced during exposure to direct sunlight at tropical and semi-tropical latitudes), the treated sample at the 100% dosage was also placed in an oven at 60ºC for 18 hours, after which the hydrocarbon concentration was determined.

The Total Petroleum Hydrocarbon (TPH) concentration in soil was determined using EPA method 9074, (mod, Mayo *et al*., 2010) a tubidimetric method which has shown to be equivalent to EPA method 418.1 for mid-range hydrocarbons in clayey, soil like materials (Adams and Ramírez, 1999; Dexsil Corp, 1998).

The stabilization treatment was also tested in contaminated organic soil. Very contaminated marshy soil was collected (0-25 cm) using a post-hole digger near the No. 4 Separation Battery in the Sánchez Magallanes oil Field (Tabasco, Mexico). The soil was let to air dry for several days to reduce the excess humidity and polyacrylamide was applied at a concentration equivalent to approx. 4 L of concentrated product per cubic meter of soil. This was recommended as 100% dosage for this very contaminated soil (>35% oil, w/w) by the product distributer. After two days samples were taken for hydrocarbon determination and the treatment was repeated. Two days after the second product application samples were collected and analyzed for TPH concentration. In addition to the hydrocarbon concentration, acute toxicity was also determined in the treated organic soil using a *Vibrio fischerii* bioassay (SECOFI, 1995; Adams *et al*., 2011). Several (8) soil samples were also collected from a nearby uncontaminated marshy area to determine background toxicity for comparison. Toxicity was calculated in Toxicity Units (TU) as the inverse proportion of Effective Concentration 50 (EC 50) as per Mayo *et al*. 2010.

Drilling cuttings were collected from the No. 5 well in the Chirimoyo oil field (Tabasco, Mexico) directly from the waste stream during the drilling process. This was treated at 100% and 150% dosage as described above for the mineral soil. In these treatments the effectiveness was not as great as for the mineral soil, and it was suspected that this was due to excess moisture in the mixture. Therefore, this process was repeated at the 100% dosage but after pre-drying the cuttings for three days before treatment.

## 3. Results and Discussion

### *3.1. General observations*

In the mineral soil, prior to treatment, the soil had a silty, slightly contaminated aspect, and brown-grey colour. After contaminating the soil, the colour was much darker, it had a strong hydrocarbon odour, and an oily aspect. The initial TPH concentration in the contaminated soil was 103,300 mg/kg (w/w, dry). After 100% dosage treatment with the polyacrylamide product the soil began to have a less oily appearance and small aggregates (approx. 3–10 mm in diameter) were observed. In the soil treated at the 150% dosage the humidity was greater during treatment, and small aggregates were not observed, but instead large clods 1–3 cm in diameter.

Prior to treatment the organic soil had a very brown-very dark grey colour and smelled like hydrocarbons and marsh vegetation in decomposition. After treatment the colour was a little lighter and the oily aspect was reduced. After the second treatment, the organic fibres started to decompose and form a drier, partially disintegrated material.

The contaminated drilling cuttings had a high initial TPH concentration (99,900 mg/kg), a grey colour, clayey appearance, and high moisture (approx. 90% field capacity). After adding the polyacrylamide product at 100% and 150% dosages it had a very muddy aspect. When the treatment was repeated but with pre-dried material, only small (0.5–1.0 mm) aggregates were observed.

### *3.2. TPH reduction and stability in treated mineral soil*

The reduction in TPH concentration according to the number of applications in shown in Fig. 1. There was no significant difference ($p>0.3$) between treatments at 100% and 150% dosage, showing that adding more product did not improve performance. However, a second dosage did enhance the reduction slightly (4%, $p=0.056$). The application number vs. hydrocarbon concentration comparison produced a potential function with an excellent correlation ($R^2=0.9998$). The extrapolation of this function to consider a third application is also shown, however the additional projected reductions are very small. None-the-less, the reduction obtained with just one application (at 100%) is sufficient to meet the goal for on-site confinement (industrial site) according to applicable legislation for some petroleum producing regions, (LDNR 1986, Rep. Venezuela 1998). The overall reduction in TPH concentration after just one application at a dosage of 100% product was high (76%) and statistically significant ($p<0.01$).

Data on the stability of the treated soil is shown in Fig. 2. As seen, following just one treatment, either at 100% dosage or 150% dosage, the material remains relatively stable and no large fluctuations are observed ($p>0.4$), either after more that a month, or after thermal treatment (60ºC, 18 hrs). These data indicate that the hydrocarbons are well stabilized in the treated material and no sudden disintegration of the stabilized product would be expected, even when exposed to high temperatures, such as might be experienced under midday sun at tropical or semi-tropical latitudes.

### 3.3. TPH reduction, toxicity and stability in treated organic soil

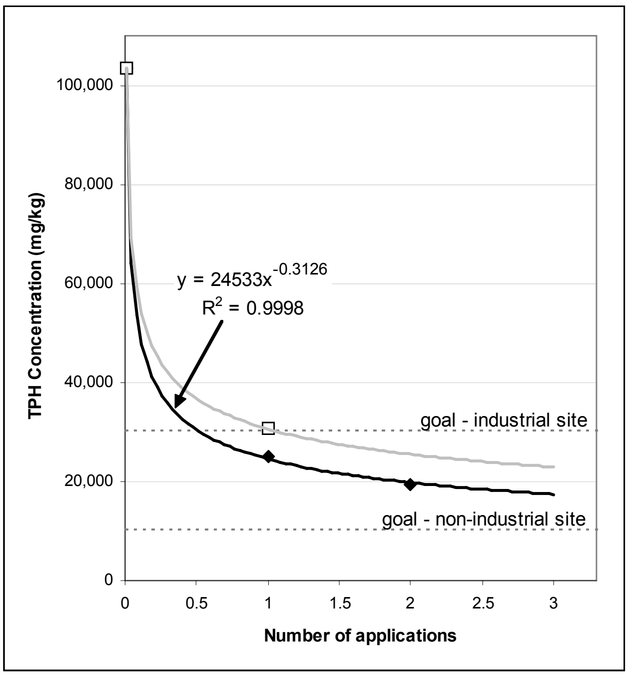


Figure 1. TPH reduction in treated mineral soil. Results from the 100 % dosage are shown in black, and from the 150 % dosage in grey.

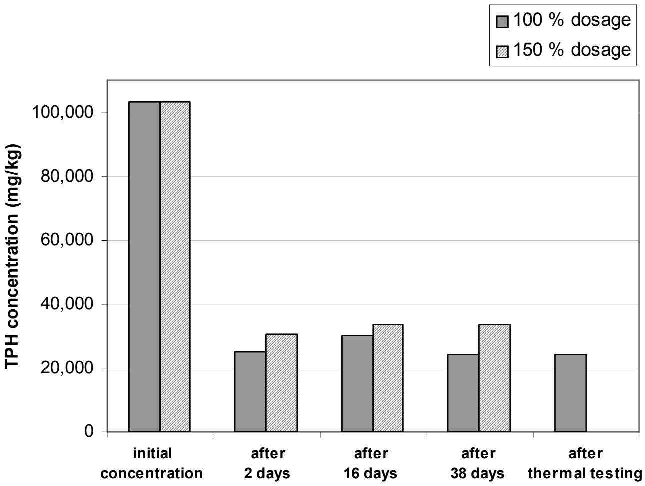


Figure 2. Stability of treated mineral soil.

In the organic soil, a relatively large reduction in TPH concentration was also observed (65%, $p<0.01$), achieving a reduction from an initial concentration of 350,900 mg/kg TPH down to 122,300 mg/kg. This is somewhat impressive considering the very high initial concentration of petroleum hydrocarbons in this soil. When the toxicity was compared to uncontaminated soil it was found to be below background levels (Fig. 3).

Even taking into account the reduction in toxicity, the final TPH concentration after just one treatment was considered to be too high. For this reason a subsequent treatment was tried. However, after the second treatment the hydrocarbon measurement increased to 189,100 mg/kg. This is probably due to the disintegration of the partially treated organic fibres and the release of the trapped hydrocarbons. Adams *et al*. 2011, observed a similar phenomenon in heavily contaminated marshy (organic) soil concomitant with the disintegration of the organic fibres in the soil. These results indicate that polyacrylamide treatment of organic soils may not provide an adequate remediation, and should probably not be used.

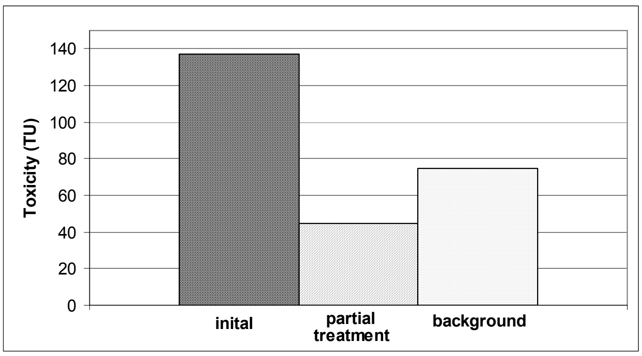


Figure 3. Toxicity reduction in treated organic soil.

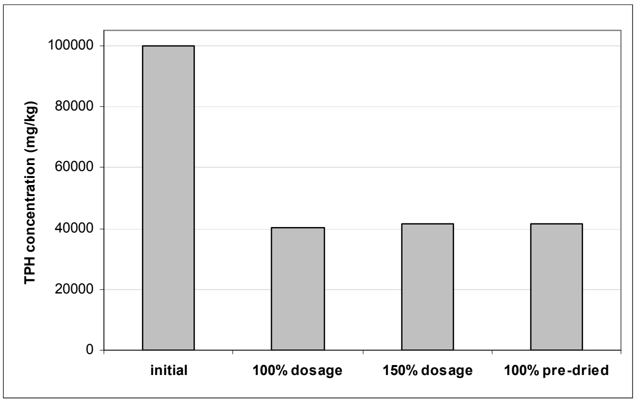


Figure 4. TPH reduction in treated drilling cuttings.

### 3.4. TPH reduction in treated drilling cuttings

The results of TPH reduction in the drilling cuttings was similar to that found in the mineral and organic soils but a little less (58-60%). There was essentially no difference between the reduction using 100% dosage, 150% dosage or pre-drying (Fig. 4). However, the size of the stabilized aggregates was much less (only about 0.5-1.0 mm in diameter) in the pre-dried material. This may be important for the long term stability of the treated product and is strongly recommended.

## 4. Conclusion

In the treatment of mineral soil, polyacrylamide application produced an important reduction in TPH concentration (76%). Treatment with a higher product concentration did not improve performance, but rather resulted in less of a decrease in hydrocarbon concentration (70%). The treated product was stable even after more than a month and after being subjected to thermal treatment. Additional treatment with the same original product concentration did improve TPH reduction, but only slightly (an additional 4%), and is probably not cost efficient. The treatment of drilling cuttings produced results similar to that found for mineral soil but the reduction was somewhat less (60%). For the material tested (starting concentration of 99,900 mg/kg) this was not sufficient for on-site confinement at an industrial site (for example, at the well pit). However, many drilling companies centrifuge their cuttings to recuperate the fluids for re-use in drilling fluid preparation (thereby recovering primary materials and reducing the production costs), and these drilling cuttings may have much lower concentrations (on the order of 60,000–70,000 mg/kg TPH, Adams 2004). With these kinds of drilling cuttings a reduction of 60% would indeed produce a remediation sufficient for on-site confinement of the treated material, and polyacrylamide treatment could be used. With respect to organic soils, the polyacrylamide treatment may reduce toxicity to below background levels, but this is not stable, and in not recommended.

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