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LEACHING OF POLYCYCLIC AROMATIC HYDROCARBONS FROM FERROMANGANESE SCRUBBER SLUDGE PLACED IN LANDFILLS

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ABSTRACT

PAH leachability of scrubber sludge from ferromanganese production was investigated by the Environmental Protection Agency (EPA) test; Toxicity, Characteristics Leaching, Proceedure (TCLP)/batch test and a column test, the latter assumed to be more representative of field conditions. The TCLP test leached totally 4000 ug/l of PAHs and 3000 of this was bound/ sorbed PAHs . The column test leached totally 1250 ug/l of which only 250 ug/l was bound , 12 times less than in the TCLP leachate. The bound PAH portion is due to sorption on leaching dissolved organic carbon or other colloids less than 0.7 um. The very high concentration of bound PAH in the TCLP leachate is an artifact due to the nature of the batch test and is therefore not a representative leaching test for this sludge. Furthermore, the bound PAHs entering the leachate and the groundwater may have a different degradation and an enhanced or facilitated mobility. This must be assessed differently than the freely dissolved PAHs.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are an increasing concern as the load of PAHs in the environment is rising and monitoring reveals that unpolluted areas can exceed "no risk" values. The carcinogenic effects of PAHs are well documented. Ecological effects of PAHs have been noted primarily in aquatic organisms which are able to accumulate these compounds. Liver tumors in several fish species, adverse affects on reproduction and impaired immune functions have been correlated with PAHs in sediments.

Generators of waste containing PAHs must fulfill many conditions before placing the waste in landfills. Testing of the waste is done to assess PAH toxicity and leachability. Leaching characteristics are then used to assess PAH mobility and fate in the subsurface. Even the very low aqueous solubility of the more carcinogenic PAH compounds is significantly higher than the drinking water limits. However, their hydrophobicity, causes them to be highly sorbed to sediment materials and thus to be relatively immobile in groundwater. Though immobile in the dissolved state, dissolved organic carbon in groundwater or in the leachate may facilitate and enhance the mobility of PAHs.

A variety of different tests and leaching criteria are being used in different countries, such as the Toxicity Characteristics Leaching Procedure (TCLP) of the US EPA, and the Standard Leaching Test in the Netherlands. The objective of this study was to characterize both free and bound PAH leachability of the wash scrubber sludge from ferromanganese production. Two test methods were compared , the TCLP and the column test.

BACKGROUND INFORMATION

As for most organic chemicals, the physiochemical characteristics of PAHs are commonly used to correlate or assess environmental properties such as mobility, sorption, volatility, carcinogenicity, toxicity, health risk, fate, degradation, bioavailability, etc. PAHs are crystalline solids with high melting and boiling points, low vapor pressures, very low water solubility and high hydrophobicity. The 16 PAH compounds listed by the US are used in this study.

Solubility

No PAH crystals are present in the environment as they are usually dissolved in complex multicomponent aqueous solutions. The appropriate solubility is that of the subcooled liquid chemical, (Sl) This solubility is considerably higher than that of the solid (Ss). At temperatures below the melting point

$$\log S_l = \log S_s + 0.01(Tm - 25) \qquad (1)$$

where Tm is the solid's melting point (K). In most environmental considerations, subcooled solubilities are generally considered to be accurate within a factor of two according to Shiu [11]. Assuming ideality in the organic phase, the solubility, Si, (dissolved concentration at equilibrium) of a compound is given by Raoult's law as:

$$S_i = X_i x S_i \qquad (2)$$

where Xi is the mole fraction of the PAH compound in the organic phase (mixture). This assumes that the activity coefficient is 1.0, remains constant, and that the compounds are sparingly soluble. Mackay [9] states that the error incurred by assuming ideality is less than the uncertainty of other parameters considered.

Sorption - Hydrophobicity

PAHs are nonpolar and have a low solubility in water. Therefore, when nonpolar surfaces are available, there is a strong tendency for the PAHs to leave solution and to sorb to the surfaces.

This hydrophobic bonding is an important factor controlling the fate of PAHs. The strength of hydrophobic bonding is measured by the octanol-water partitioning coefficient, Kow.

Three phases make up the equilibrium distribution of hydrophobic chemicals in a leachate or a soil/groundwater system: freely dissolved PAHs, as determined by the solubility, PAHs sorbed on solid matter and sorbed PAHs on mobile suspended matter such as organic carbon, according to partitioning coefficients, Geschwend [6] and Chiou [1].

If equilibrium is achieved for a particular leachate, a specific dissolved concentration of each component in the water phase will be achieved. These are the free concentrations. In addition, if "dissolved" organic colloids are present, there can be an enhancement in apparent solubility, as PAHs are sorbed on these colloids. These are the bound PAH concentrations. Free and bound PAH concentrations on colloids in the leachate can be estimated if the following is known:

a. Total PAH concentrations, which include both free and bound, for each compound (measured by GC/MS)
b. Dissolved organic carbon (DOC) of the leachate.
c. Liquid (subcooled) solubility of the PAH compounds.

The calculation procedure includes:

a. Estimate the composition, moles and mole fraction of PAHs in the leachate.
b. Calculate the free PAH concentrations according to Raoult's law.
c. Calculate Kdoc (partitioning between free and colloidal phase) for the most hydrophobic PAHs and establish the regression logKdoc = alogKow + b, assumed valid for all PAHs.
d. With Kdoc, DOC and total PAH the free and bound PAHs can be calculated for each compound.

Another method is by iteration where the calculations of free and bound PAH are based upon Raoult's law and the fact that the measured total PAH concentration, Ct is equal to free and bound PAH, Cf and Cb respectively.

$$C_f = X * Sl \quad \text{(Raoult's)} \qquad (3)$$

$$X = m_w/MW \quad \text{(mole fraction)} \qquad (4)$$

$$C_t = C_f + C_b \qquad (5)$$

where m_w is the molecular weight of the PAH compound and MW is the molecular weight of the organic phase in the leachate. The iteration establishes the converging values of Cf and Cb.

MATERIALS

Elkem a.s, an international ferro alloy producer has, for this research project, made sludge available from their Ferromanganese plant in Sauda, Norway.

The smoke from closed furnaces is trapped by scrubbers. After flocculation, sedimentation and dewatering, the sludge is placed in landfills. Coal and coke, and the tar - baked electrodes are the sources of PAHs. In addition PAHs are formed by pyrolysis in the furnace under incomplete combustion.

In the column test, the hydraulic conductivity of the sludge was found to be 1.6x10E-5 to 1x10E-6 cm/sec with a dry bulk density of 1.5 g/cm3. The total amount of PAH is about 0.01 g/g solid. The organic carbon content is 6 % of dry weight and is assumed to be mostly large molecules of refractory black carbon. The sludge is heavily mineralized and is highly alkaline with pH > 11.0. The largest inorganic components of the sludge are potassium, sodium, bicarbonate and sulfate.

LEACHING TESTS AND CRITERIA

The Toxicity Characteristic Leaching Procedure,(TCLP, EPA. SW - 846) is the primary procedure adopted for the batch tests in this study. A batch of 50 g dried sludge and 1 l deionized water, equivalent to liquid to solid ratio of 20 is tumbled head over head for 20 hours at 30 rpm. The liquid/solid is separated by pressure in a zero head space cell with 0.7um glass fiber filter. According to Newcomer [10] this method has been noted for its ease of operation, low cost, and low experimental variation.

The column extraction method involves the continuous flow of water through a fixed bed of solid waste. Leachate generated by the column method is more representative of actual field conditions; however, the method is not readily applied in a regulatory framework because of its long duration and often poor reproducibility, as stated by Environment Canada,[3].

For both the batch and column tests, the liquid to solid ratio (L/S) is a measure of (L kg) mass of leachant or percolation water L which has been in contact with (S kg) waste material.

A stainless steel column 30 cm long with an internal diameter of 12 cm was packed with sludge with a water content of 75 % and a wet density of 1.53 g/cm3 by weight. Deionized water was forced upward through the column at a constant flow rate of about 1 l/day.

ANALYTICAL METHODS

The PAHs were extracted from 1 l samples and analysed according to EPA, SW - 846. The dichloromethane extracts were analyzed on a Hewlett Packard 5890 gas chromograph equipped with a 5970 Mass Selective Detector and a 30 meter x 0.25 mm fused silica DB - 5 column.

Dissolved organic carbon (DOC) was measured using a Dohrman Carbon Analyzer. This instrument converts the organic carbon to carbon dioxide (CO_2) by combustion for measurement by a non - dispersive infrared analyzer. The sample is pretreated with acid to remove inorganic carbon.

RESULTS AND DISCUSSION

The equilibrium batch test showed that both free and bound PAHs and dissolved organic carbon (DOC) reached equilibrium in two stages, confirming the theory of Karickhoff [7]. Of the total dissolved and individual PAHs and DOC, about 75 to 85 % leached rather rapidly, in 1 hr or less, and the remainder, the second stage, took more than 2 days.

Fig.1 shows the results of the sequential batch test, where free and bound PAHs are shown for each compound and each sequence. Almost no bound PAHs were detected among the least hydrophobic compounds. The percentage of bound PAH to total PAH increases with increasing Kow and for Benzo(a)anthrachene and heavier compounds the bound fraction is close to 100 % of the total PAH.

An aqueous GC/MS analysis measures the total PAH content, which includes all PAHs; free, bound and pure phase. The known liquid (subcooled) and solid solubilities for individual compounds are valuable tools in assessing the overall results of a PAH analysis. Fig. 2 shows the liquid and solid solubilities for the individual PAH compounds. On this figure the total PAH and the free calculated PAH concentrations from the TCLP test are also plotted. Area (1), shaded on the figure, indicates total concentrations of PAHs in the leachate which are higher than the individual PAH solid solubilities. This is only possible if the excess is PAHs in bound or sorbed state or pure phase chemicals. In this case it is believed to be bound PAHs. Area (2) on the figure shows that the free dissolved Benzo(a)fluoranthene concentration is higher than its solid solubility. This is physically impossible and could be due to analytical or calculation error.

The total free and bound PAHs are also plotted against numbers of agitations in Figure 3. The free PAHs remain fairly constant for each test in the sequences. The concentrations of the bound PAHs and DOC decrease quite rapidly and then slowly after the third and second agitations, respectively.

At this stage of testing the PAH leachability of the sludge, according to TCLP, is very high. To provide a more representative measure of leachability, the column experiment was run for 6 months. The results are summarized in Figure 4. The free PAHs increase initially with increasing leaching and seem to reach a maximum concentration of about 1050 ug/l after 20 l of leaching. The bound PAH decreased gradually from an initial value of 500 ug/l in the pore water to about 300 ug/l after about 15 liters of leaching, to less than 200 ug/l after 150 liters (6 months). The initial DOC concentration was quite high at 148 mg/l . It then decreased rapidly to 18 mg/l after 8 days of leaching then declined slowly to 8 mg/l.

<u>Comparison of Batch and Column Test</u>

It may be incorrect to compare leaching data directly for such different tests. The two leachates appeared very different also, the batch test leachate was greyish and cloudy while the column leachate was yellow and clear in the beginning, and remained very clear throughout the test. Furthermore, the TCLP test leaches about 200 times more PAH than the column test of their respective test samples. However, by using L/S criteria and corresponding cumulative concentration or average concentration the two tests are compared, Environment Canada, [3]. Calculated Kdoc values plotted against the compounds Kow value from the batch tests and the column test and then regressing these values gave the following average Kdoc-Kow linear relationships:

$$\text{Batch: } \log K_{doc} = 1.19 \log K_{ow} - 0.75 \qquad (6)$$

$$\text{Column: } \log K_{doc} = 1.19 \log K_{ow} - 1.20 \qquad (7)$$

The batch test, appears to have Kdoc values, about 3 times higher than for the column test. For some of the more hydrophobic compounds the difference is as high as 12 times.

For the batch test the bound fraction of PAH is 1233% larger than in the column test. The difference in concentrations of free PAHs is only 36%. For the dissolved organic carbon, DOC, the trend is reversed and the column test leaches 26% more than the batch test.

Except for the bound PAHs these data are similar considering the uncertainties involved. It is difficult to explain why the TCLP test leaches much more bound PAHs but less DOC. To evaluate this more closely the average concentrations for each compound, at L/S = 20, are shown for both tests in Fig.5. The TCLP test clearly shows that the bound PAHs for the compounds Phenanthrene to Dibenzo(a,h)anthracene, make up the difference. The least hydrophobic compounds are, on the other hand, similar. Normalizing the bound PAHs to the DOC, the ratio of cumulative release of bound PAHs and DOC is 0.22 for the TCLP test and only 0.012 for the column test. This shows that the TCLP DOC has 18 times larger adsorptive apacity. The TCLP batch test with its agitation seems to "kick off" organic carbon, possibly larger and heavier organic molecules and other colloids, which can bind and attract the more heavy PAHs.

The TCLP test is believed not to be a representative method for quantifying the PAH leaching of ferromanganese sludge. About 75% of the leached PAHs are bound and this is believed to be an artifact of the method.

However, bound PAHs entering the groundwater subsurface, already adsorbed on organic carbon of colloidal size, may have very important implications. They may undergo less sorptive retardation. According to several studies like Stucki, [12]these bound PAHs may also be protected from biodegradation. The organic colloids may also be so large that they may not pass through the aquifer pores. The extent of their enhanced mobility in the groundwater is very uncertain and no comparable cases have been found in the literature. Cases of facilitated transport have been reported and research work shows that for, hydrophobic organic compounds of Kow = 5 to 7, the retardation is reduced by a factor of 2 to 5. Enfield [2] and Magee [8] found that this effect appears to be strongly dependant upon the amount of DOC as the bound portion increases with increasing DOC.

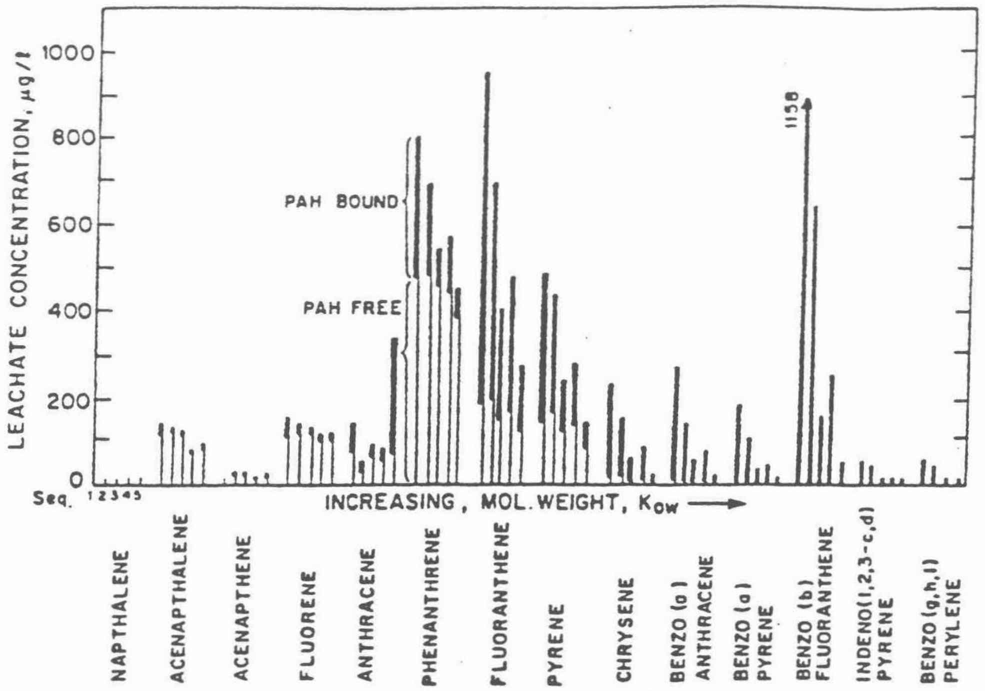

Fig. 1. Serial or sequential batch test, PAH concentrations free and bound for each compound and sequence

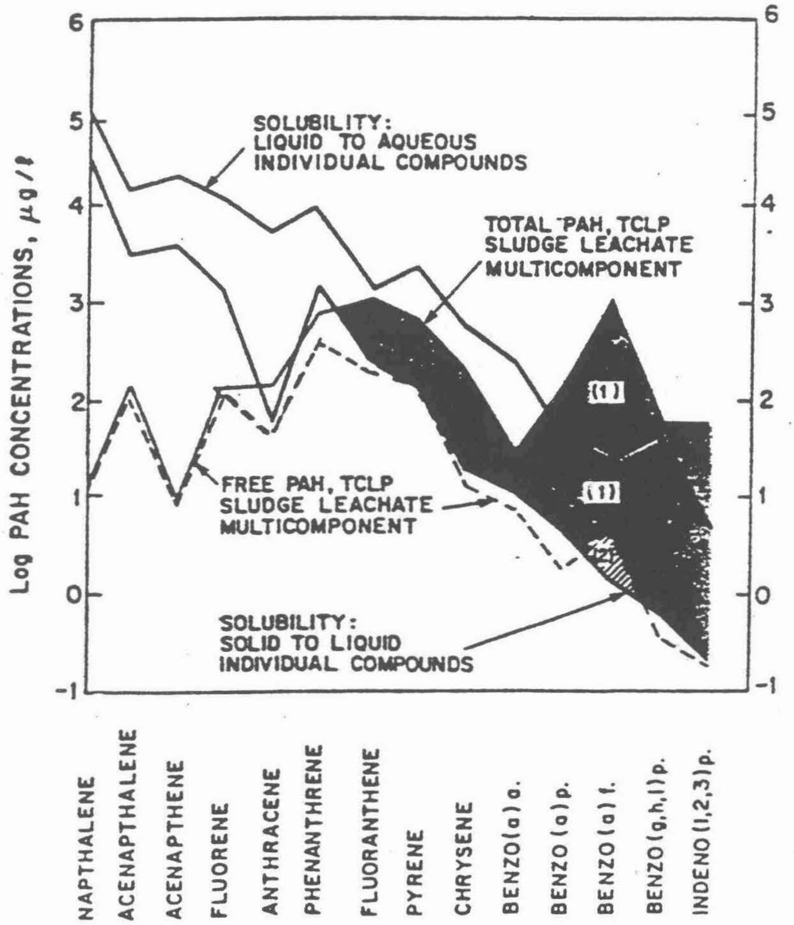

Fig. 2. Solid and liquid PAH solubilities and observed PAH concentrations in the leachate from the TCLP test versus individual PAH compounds..

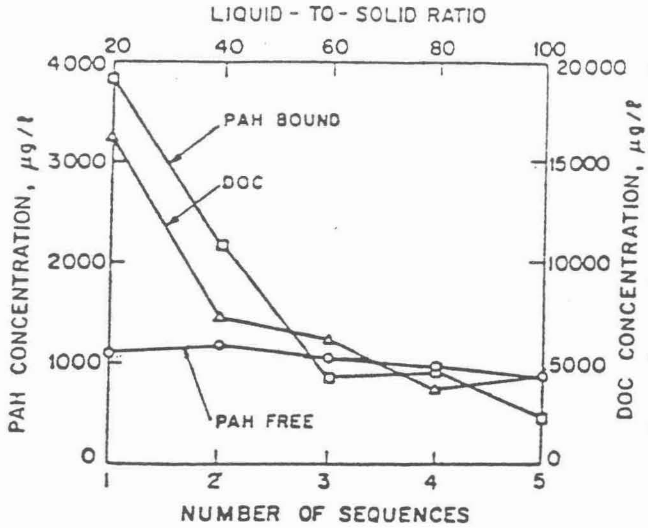

Fig. 3. Serial or sequential batch test, PAH free and bound and DOC versus liquid to solid ratio.

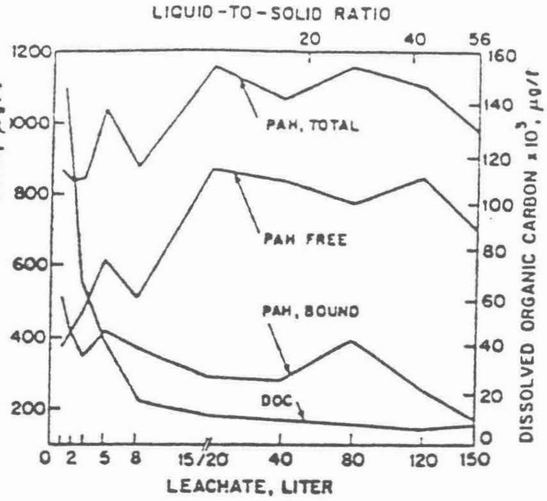

Fig.4. Leaching of free and bound PAH and DOC during the column test versus liquid to solid ratio and amount leached.

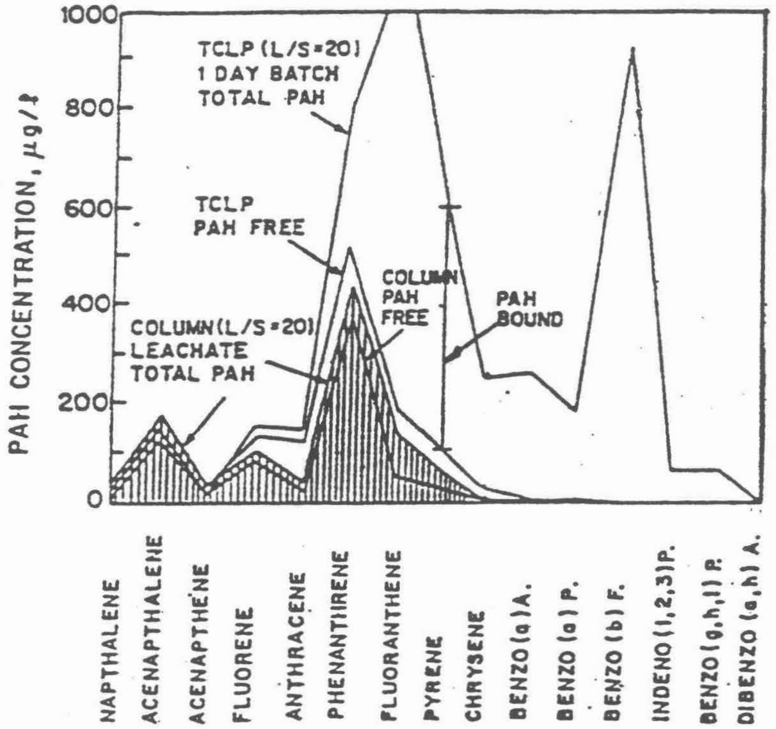

Fig.5. Free and bound PAH concentrations from the TCLP test and the column test for each individual compound.

CONCLUSION

The TCLP test appears to release, besides the freely dissolved PAHs, large amounts of PAHs adsorbed (bound) on dissolved organic carbon (DOC). This is especially significant for the more hydrophobic compounds.

The column leaching test, which is probably more representative of field conditions, showed significantly less bound PAHs in the leachate than did the TCLP batch test.

The dissolved organic carbon, DOC, appears to be very different in these two tests. The DOC of the batch has larger adsorptive capacity and more hydrophobic PAH compounds are attracted by DOC into the leachate. The column leachate carry a small fraction of PAHs and only a small amount have been desorbed from the sludge. This is believed to be due to the nature of the test and the binding characteristics of the released DOC.

The TCLP test is not a representative method for quantifying the actual PAH leaching of ferromanganese sludge, This may also be the case with similar wastes.

The bound PAHs are entering the subsurface in a « prefacilitated transport condition». This is very different from the free PAHs and requires separate assessment with regard to subsurface mobility and degradation.

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