COMBUSTION OF CRUDE OIL SLUDGE CONTAINING NATURALLY OCCURRING RADIOACTIVE MATERIAL

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ABSTRACT

The characteristics of crude oil sludge from the crude oil terminal are very unique because it contains both heavy metals and also Naturally Occurring Radioactive Material (NORM). As a result, the Department of Environmental (DOE) and the Atomic Energy Licensing Board (AELB) considered it as Scheduled Wastes and Low Level Radioactive Waste (LLRW) respectively. As a Scheduled Wastes, there is no problem in dealing with the disposal of it since there already exist a National Center in Bukit Nanas to deal with this type of waste. However, the Center could not manage this waste due to the presence of NORM by which the policy regarding the disposal of this kind of waste has not been well established. This situation is unclear to certain parties, especially with respect to the relevant authorities having final jurisdiction over the issue as well as the best practical method of disposal of this kind of waste. Existing methods of treatment viewed both from literature and current practice include that of land farming, storing in plastic drum, re-injection into abandoned oil well, recovery, etc., found some problems. Due to its organic nature, very low level in radioactivity and the existence of a Scheduled Waste incineration facility in Bukit Nenas, there is a potential to treat this sludge by using thermal treatment technology. However, prior to having this suggestion to be put into practice, there are issues that need to be addressed. This paper attempts to discuss the potentials and the related issues of combusting crude oil sludge based on existing experimental data as well as mathematical modeling.

INTRODUCTION

Recent study made by Hamrah and Amran (1996) shows that, there were more than two hundred oilrigs in operation throughout Malaysia, extracting the crude

oil, offshore of Terengganu, Sabah and Sarawak. Crude oil sludge are generated during the extraction of crude oil from the underground oil reservoir to the oilrigs, the separation process at the oilrigs, its storage at the crude oil terminal (known as Crude Oil Terminal Sludge, COTS) and its transportation from the crude oil terminal to the refineries (known as Tanker Sludge, TS). About 1450 tons of COTS is generated annually and about 16 000 tons of these sludge have been accumulated and stored at the Malaysian crude oil terminals up to the year 1996 (Puad and Wahab, 1996). TS are generated as a result of cleaning sea-going vessels carrying crude oil at various ports cleaning facilities. (One of this facility in Malaysia is the Malaysian Shipyard Engineering, MSE, Pasir Gudang, Johor). The amount of sludge accumulated at MSE is not exactly known, however, the 6 000 ton storage capacity sludge storage building seems to be full (Omar et al. 1997). These sludge cannot be disposed freely without proper control because they are considered as low level radioactive waste (contains NORM, such as U-238, Th-232, Ra-226 and Ra-228) by the AELB and Scheduled Waste (contains heavy metals such as As, Pb, Cd, Cr and Organics) by DOE.

The current method of disposal, such as land farming is not recommended and will have long term impact to the environment (Smith et al. 1996), whereas storage practices in plastic drums does not warrant an ultimate solution. Due to its organic nature, there is a move to treat this sludge by using thermal treatment technology but prior to this, a study has to be carried out to determine the behaviors of the various elements present in the sludge especially that of NORM and heavy metal.

The partitioning of metals depends on the type of metals and its physical-chemical properties such as boiling point and vapor pressure (William, 1999). Thus high vapor pressure and low boiling point metals and their compounds, such as Hg and Cd, most likely are found in gas phase. On the other hand, low vapor pressure and high boiling point metals such as Fe and Cu, most probably found in the bottom ash. The speciation of the metals in the incinerator off-gas is strongly influenced by the presence of compounds of sulfur, carbon, nitrogen (William 1994) and halogens (Jost 1997, William 1994, Buenkens 1985) during combustion and gas cooling. The extent of evaporation of heavy metal during thermal treatment depends on complex and interrelated factors such as operating temperature, oxidative or reductive conditions (Buenkens 1985, Carrol 1994). During thermal treatment a fraction of heavy metals and their compounds will volatilize and subsequently condense on nuclei and form metal particulate during the cooling of the flue gas (Ho. et al. 1993).

Recent bibliography reports made by Smith et al. (1997) showed that no single literature described the treatment of oil sludge containing NORM by thermal treatment technology. Thus the partitioning of NORM in the COTS undergoing

thermal treatment is not known; hence no comparison can be made. However, it is believed that it tends to follow the partitioning of heavy metals described above. It is believed that it follows the behaviors of NORM present in TS when incinerated and coal or peat when combusted in power plant for the energy production. This paper will report the studies on the partitioning of Uranium-238 (U-238), Thorium 232 (Th-232), Radium-226 (Ra-226) and Radium-228 (Ra-228) from the NORM family in crude oil sludge when undergoing thermal treatment. The selection of NORM radio nuclides was based on their occurrence in the oil sludge, in which Ra-226 and Ra-228 are more dominant compared with others, while U-238 and Th-232 is the parent of Ra-226 and Ra-228 respectively. This study will also be based on two parameters such as temperature and time, on the assumption that it is in fully oxidative condition. The influence of halogen etc is assumed to be insignificance. From this experimentation data, a mathematical modeling was developed and a simulation work was done on typical incinerator environment. Finally, the simulated result was compared with other works found in the literature.

EXPERIMENTAL

The raw oil sludge used in this study was taken from one of the crude oil terminal in Malaysia. Oil sludge samples were placed in several plastic drums, transported and stored at the Combustion Research Center, Universiti Kebangsaan Malaysia (UKM). The initial concentration of U-238, Th-232, Ra-226, Ra-228, in the oil sludge is shown in Table 1 (Puad et al. 1999). The overall characteristics of the oil sludge have been reported elsewhere by Puad et al. (1999).

TABLE 1 The Concentration of U-238 (ppm), Th-232 (ppm), Ra-226 (Bq/kg), Ra-228 (Bq/kg) in the oil sludge.

U-238	1.21 - 2.59	Ra-226	25.00 - 96.00	Th-232	3.51-11.05
Ra-226	25.00- 96.00	Ra-228	26.00 - 123.00		

The raw sludge was then combusted in a fixed bed furnace at temperature of 100, 300, 500, 700 and 800 ^{0}C and for a period of 30, 60, 90, 120 and 150 minutes at each temperature using electric furnace model N7 NABER industries of Enbau. The ash produced was then analyzed for the elemental concentration. The concentration of U-238 and Th-232 in the raw sludge and ash were determined using Neutron Activation Analysis (NAA) technique, at MINT. Ra-226 and Ra-228 concentration in the oil sludge and ash were analyzed using gamma spectroscopy system SG1 and SG2, Tennelec. Before measurement was made, the

sludge and the ash were packed in 350 ml sealed plastic container for at least 20 days so that the U-238 and Th-232 and their progenies were at secular equilibrium stage. The mass of the sludge and its subsequent ash were measured using an analytical balance. The extent of partitioning was calculated in terms of percent volatilization.

MODELING AND SIMULATION

In so far no literature cited that discusses the modeling of NORM undergoing thermal treatment. However, it is believed that their behavior resembles that of heavy metals. Experimental works by Ho et al. (1993) suggests that the volatilization follows first order kinetics. Based on the above observation, a volatilization equation describing the above process is developed. The equation is as follows:

$$Q_e = 1 - e^{-k_e t}$$

where, Q_e = Volatilization rate, %

k_e = A constant, a function of the element and temperature, min^{-1}

t = Period of combustion, min.

From this volatilization equation, a simulation work is developed to predict the NORM partitioning in the bottom ash and filter ash. Results from this simulation are then compared with other works found in the literature. It is assumed that all volatile is condensed onto particulate and fully collected in the filter bag i.e. no fly ash is generated. Only one set of temperatures is tested for simplicity (800 ^{0}C). The solid residence time in the incinerator is large (>10hrs).
The bottom ash emission and filter ash production is assumed to be about 70 % (based on proximate analysis) and 1-3% (Muhd Noor. M. Y. & Mohamad Puad H. A, 1999) of the waste load respectively unless mentioned in the literature.

RESULTS AND DISCUSSIONS

Figures 1 through 4 show the partitioning of NORM when undergoing thermal treatment. U-238 demonstrates a unique behavior compared to Ra-226, Ra-228 and Th-232. It could be seen that U-238 de-volatilised (70%) more than other radionuclides and has a clear temperature and time demarcation at 500 ^{0}C and 60 minutes respectively. The de-volatilization is at maximum in the temperature range of 700 - 800 ^{0}C or at 120 to 150 minutes. This finding is in agreement with the

work of Omar et al. 1997. It is interesting to observe the above phenomena, as U metals is known to have high boiling point (3925 ^{0}C), this maybe due to the existence of U salt [e.g. $UO_2(NO_3)_2.6H_2O$ and UCl_4] in the sludge instead of U metals of which U salt was known to have very low boiling point [($UO_2(NO_3)_2.6H_2O$ = 118 ^{0}C and UCl_4 = 792 ^{0}C)] (Jacob 1986). Further investigation is warranted to confirm this claim.

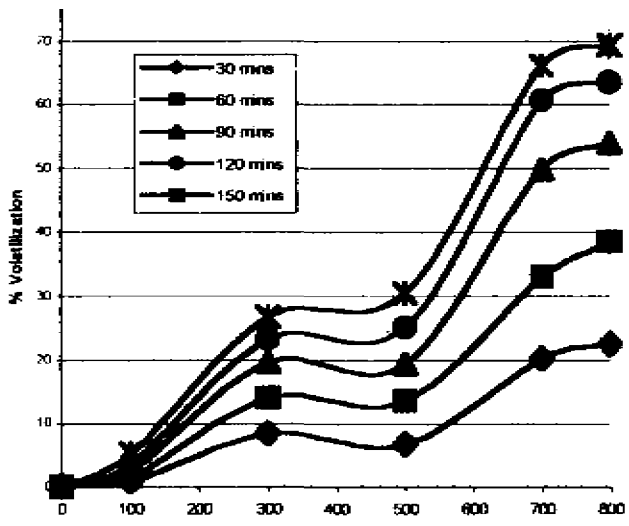

FIGURE 1 % Volatilization U-238 VS Combustion Temperature (^{0}C)

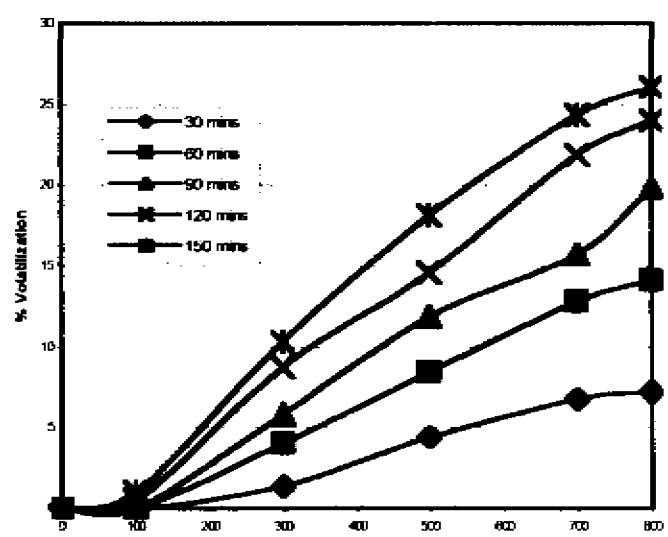

FIGURE 2 % Volatilization Ra-226 VS Combustion Temperature (^{0}C)

Ra-226 and Ra-228 begin to volatilize above 10 % when the temperature and the heating time are above 500 ^{0}C and 90 minutes respectively. It is interesting to note that, above 800 ^{0}C and 150 minutes, the de-volatilization of Ra-226 and Ra-228 continue to increase. The partitioning of Ra undergoing thermal treatment is comparable to Ca and Ba, because they are in the same chemical species, group II, whose partitioning pattern is well established i.e. de-volatilized up to 30 % at incineration operating temperature of 800 - 850 ^{0}C (Ho et al. 1993). Just for comparison, Ba in municipal solid waste when combusted in kiln incinerator, volatilize in the range of 1 to 23 % (Carol 1994) while in our finding show that Ra-226 and Ra-228 volatilize in the range of 2 to 24 %, which is surprisingly almost identical.

Th-232 seems to behave like Ra-226 and Ra-228 in term of percent of volatilization with respect to temperature and time, which is in the range of 2 to 25 %. Here also the volatilization rate of Th-232 continues to increase above 800 ^{0}C and 150 minutes. However the partitioning of Th is not found in literature, thus, no

comparison can be made. For the partitioning NORM, it is found that Ra-226, Ra-228 and Th-232 behave in one identical manner but U-238 is completely different.

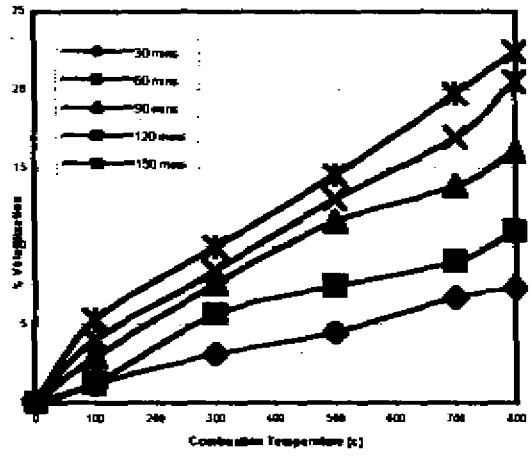

FIGURE 3 % Volatilization Th-232 VS Combustion Temperature (^{0}C)

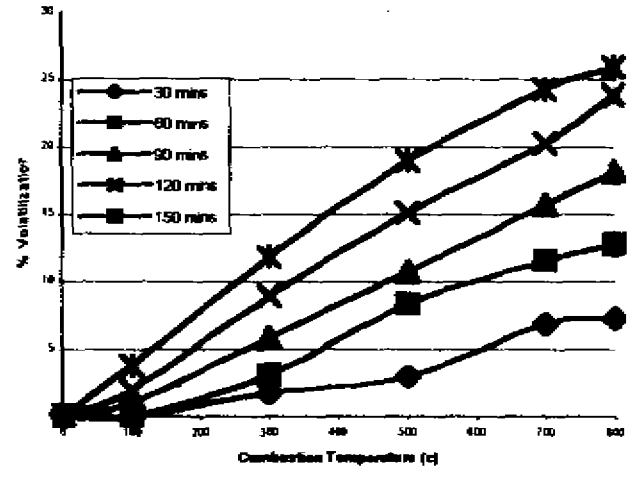

FIGURE 4 % Volatilization Ra-228 VS Combustion Temperature (^{0}C)

The proposed model was then compared with these experimental results as shown in Figure 5 through 8. The degree of variation is found to be very small less than 5 % except for U-238 at 500 ^{0}C, this is due to the chemical formation of U in COTS, which has been explained, in the previous paragraph. Thus, the model does describe the volatilization process.

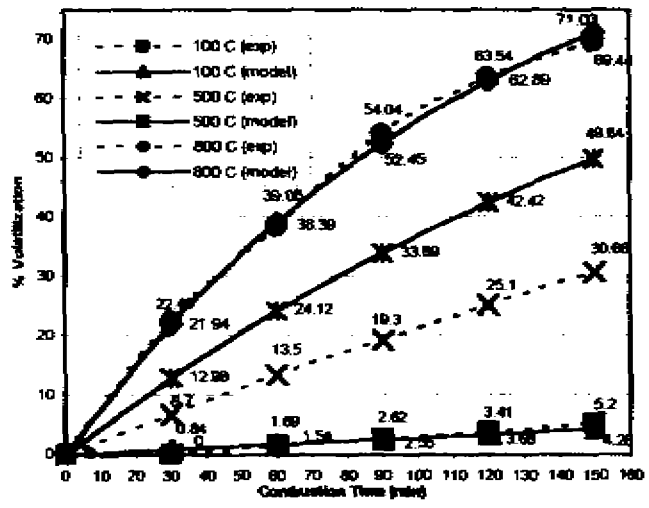

FIGURE 5 Comparison model & Experimentation U-238

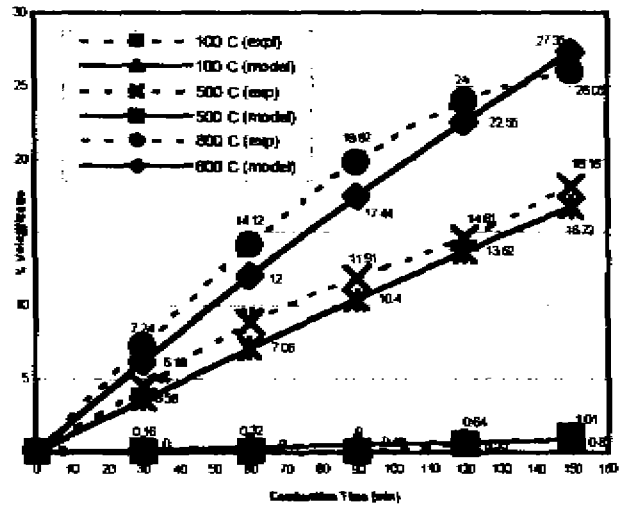

FIGURE 6 Comparison model & Experimentation Ra-226

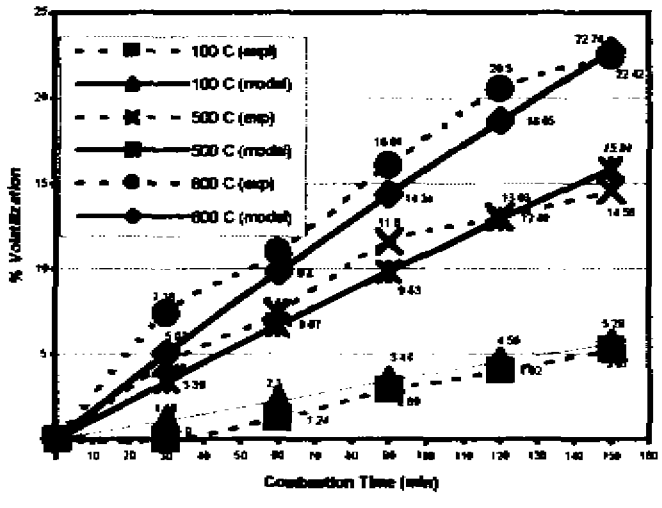

FIGURE 7 Comparison model & Experimentation Th-232

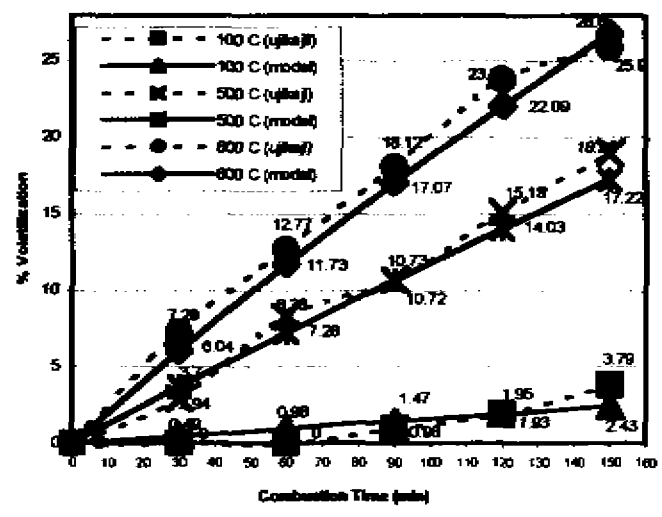

FIGURE 8 Comparison model & Experimentation Ra-228

In 1997, Malaysian Institute for Nuclear Technology Research (MINT), (Omar et al. 1997) has done a preliminary research on the behavior of NORM from TS when undergoing thermal treatment and found that the concentration of NORM increases more than 100 times if compared with the raw sludge. The majority of the radionuclides are collected in the filter ash. No detail account was made as to the factors influence the above finding. Figure 9 shows the partition of U-238, Ra-226, Th-232 and Ra-228 from a simulation work compared to the measured value at the MSE incinerator in Johor.

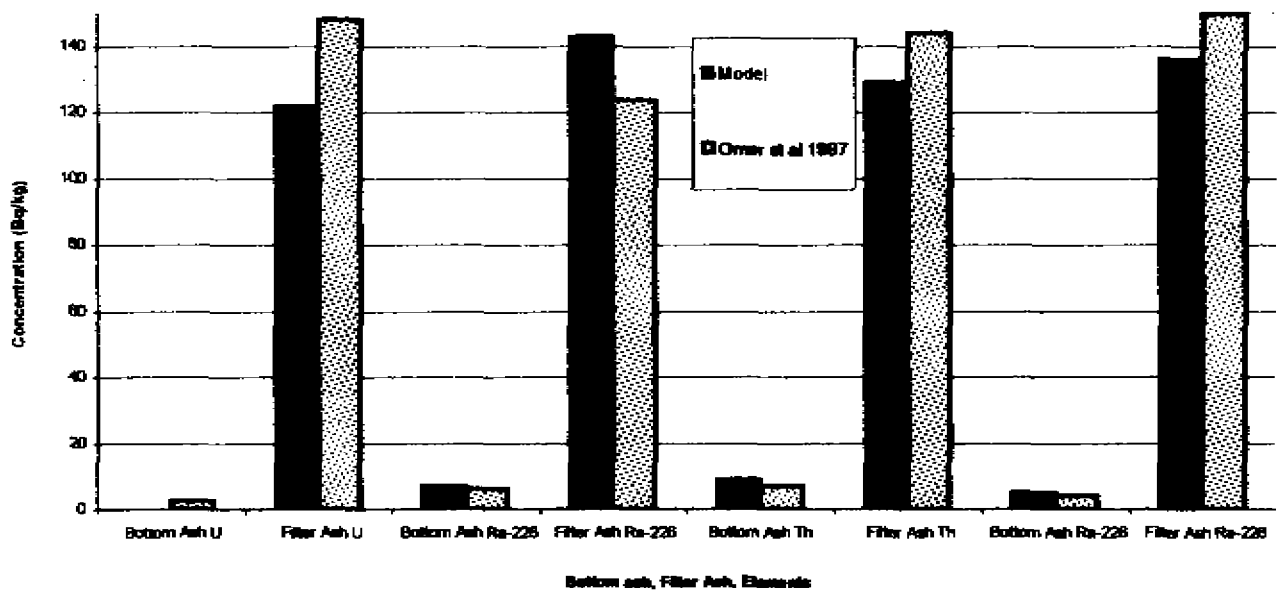

FIGURE 9 Comparison Model with Omar et al. 1997

A research work done on the NORM concentration on coal ash by Papastefanou (1996) at one of the Greek coal-fired power plant showed that there was an increase in NORM concentration 2 to 3 times before and after the combustion. Here also the majority of the radionuclides were collected in the filter ash. Papastefanou (1996) however made no explanation about the above phenomena. Figure 10 shows the partition of Ra-226 from a simulation work compared to the measured value at the Greek coal-fired power plant.

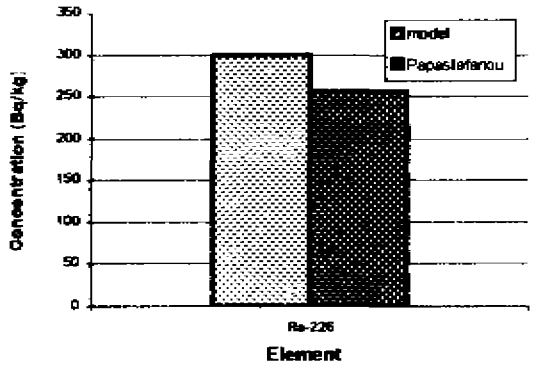

FIGURE 10 Comparison Model With Papatefanou 1996

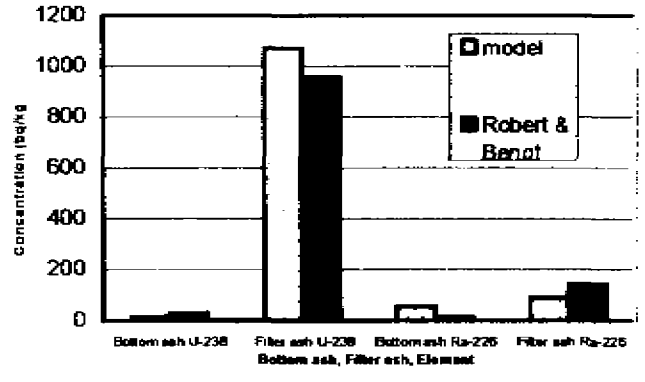

FIGURE 11 Comparison Model with Robert 1992

Research performed by Robert & Bengt (1992) on the peat ash at one of the peat-fired power plant in Sweden also shows that there was an increase in NORM concentration 2 to 10 times before and after the combustion. Here again the majority of the radionuclides are collected in the filter ash. Robert & Bengt (1992) explained that the majority of radionuclide found in the filter ash was U-238. This finding is in agreement with our works. Figure 11 shows the partition of U-238 and Ra-226 from a simulation work compared to the measured value at the Sweden peat-fired power plant.

Surprisingly, from the above comparison shows that, the order of magnitude agrees to each other although the raw materials are totally different from each other, showing that the suggested model bears some credit, despite of a gross estimate and neglect of certain controlling parameters. From this comparison, it is believed that, the above equation can also be used to predict the volatilization rate of NORM contain in other materials such as coal, peat and TS when combusted at certain temperature and time.

CONCLUSION

From this study, it was found that the percentage of volatilization varies from 2 - 70%, which is a function of the elements concerned, temperature and time.

Uranium seems to volatilize much more than the rest of radionuclides. Under the present conditions and assumptions, U-238 significantly de-volatilized above 500 ^{0}C or 90 minutes and reach maximum at above at above 700 ^{0}C or 120 minutes. This finding is in close agreement with the result report in the literature. The partitioning of other radio nuclides under thermal treatment shows that the de-volatilization continue to increase above 800 ^{0}C and heating time of 150 minutes which follows general trends found by other workers.

Further processing of oil sludge, typically by thermal method resulted in enhancement of NORM concentration. Studies made to investigate this phenomena showed that higher temperature (>500 ^{0}C) and longer exposure time (60 Minutes) promoted radio nuclides partitioning significantly. Typical to incinerator environment high furnace temperature (850 ^{0}C) and very long solid residence time (>10 hrs), the radionuclides de-volatilization is very substantial. From this partitioning study, it could be suggested that Low Bed Temperature (max 500 ^{0}C) bed combustor coupled with second stage gas phase combustion might work to reduce the metal de-volatilization.

From this study, it was also found that the volatilization process for NORM follows first order kinetics.

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