MY9800973

Radioactivity partitioning of oil sludge undergoing incineration process.

Muhamat Omar, Suhaimi Hamzah, Muhd Noor Muhd Yunus

MINT, Malaysia.

July, 1997

Oil sludge waste may contain Naturally Occurring Radioactive Materials (NORM), thus it is a controlled item under the Atomic Energy Act (Act 304) 1984 whose radioactivity content shall be subjected to analysis. Apart from that the treatment method also shall be approved by Atomic Energy Licensing Board (AELB). Thus, an analysis of the oil sludge for MSE fluidized bed incinerator was conducted to comply to the above requirements using various techniques. Further screening analysis of filter ash as well as bed material were done to study the effect of radioactivity partitioning when incinerating the sludge. This paper highlights the analysis techniques and discusses the results with respect to the radioactivity levels in various samples and the fate of radionuclides subjected to the above process.

1.0 Introduction

Oil sludge waste in Malaysia come from offshore oil production or shipyard services operations. The waste may contain a varied degree of Naturally Occurring Radioactive Materials (NORMs) and thus the storage, treatment and disposal is controlled by Atomic Energy Licensing Board (AELB) under the Atomic Energy Licencing Act (Act 304) 1984 following the relevant Guideline (LEM/TEK/30 Sem. 2, September 1996). Apart from this, oil sludge is also considered as hazardous waste in accordance to Scheduled Waste Act (Schedule Waste), 1989, thus it is also subject to the control of the Department of Environment (DoE).

An incineration facility was constructed by ANI Engineering Sdn. Bhd. for Techno Indah/Malaysia Shipyard Engineering (MSE), Pasir Gudang, Johor to treat oil sludge collected by MSE from shipyard services operation. MINT has been requested to analyse the oil waste as to the level of radioactivity in it as part of the AELB requirements. MINT is also to screen the level of radioactivity in the bed material as well as the filter ash, to investigate the possible build up in the level of radioactivity in the bed material and filter ash, as had been shown to occur in coal power plant combustion (Tadmor, 1986).

2.0 Experimental details

2.1 The Incineration Plant

The primary objective of the plant is to dispose of the oil sludge in a clean and environmentally acceptable manner, via incineration, while recovering energy from the sludge. The plant comprises a single chamber, fluidised bed combustor (FBC) having a capacity of 1.6 t/hr at 17,400 kJ/kg heat capacity. The calorific value of the sludge vary up to 40,000 kJ/kg(gross) [David, 1996]. The above average calorific value of 17,400 kJ/kg was based on the following composition (w/w %): Oil content: 40%, Water content: 30%, Solid content: 30%.

The oil sludge was removed from the tankers in plastic bags and transported to the sludge storage building, having a 6000 ton storage capacity. The material was fed to shredders, where the bags and any oversize material were shredded to ensure that they would pass through a pump. Two helical rotor pumps fitted with variable speed drives will feed the material to the revolving fluidised bed furnace where it will be fully burnt to produce hot gases for energy recovery in a boiler. The boiler is of the water tube type producing high pressure superheated steam, 12,000 kg/hr at 30 bar, suitable for use in steam turbine.

The gases passing out of the boiler contained dust which were removed by a bag filter unit before the gases were discharged to atmosphere by an induced draught fan. The furnace were fitted with equipment to inject limestone to control acid gas emissions to the European Community standard. The power generation equipment comprises of a fully condensing turbo generator set with wet type cooling tower and was a standard package unit from a proprietary manufacturer. This unit could generate up to 1.5 MW(E) power onto the site distribution grid adjacent to the plant. Figure 1 shows a schematic layout of the plant.

In consistance with the work of Tadmor (1986), the following terminology is used, with respect to the plant above: **Filter ash** is the ash collected by the bag filter whereas **fly ash** is the ash that is not able to be collected by the bag filter, the so called sub microns particulates. **Bed material** is referred to the sand and ash materials deposited and removed from time to time from the fluidised bed incinerator in order to control the bed depth.

2.2 Sampling

The sampling was done by Techno-Indah as advised by MINT. Ten (10 Nos.) oil sludge samples, each contained in a 350 ml plastic bottle, were taken at ten representative locations in the storage pit. Two (2 Nos.) samples each for filter ash and fluidised bed material were also taken to check the level of radioactivity. All samples were placed in sealed plastic bags, transported by land on the same day of collection. In the laboratory, the samples were stored in a safe cabinet at ambient temperature with appropriate labeling done on them.

2.3 Methods of analysis

The Uranium (U-238) and Thorium (Th-232) radionuclides were measured by using Neutron Activation Analysis, whereas the other radionuclides were measured using gamma spectroscopy.

2.3.1 Analysis of Uranium and Thorium

Samples (0.2 - 1.0 g) were accurately weighed in pre-cleaned polyethylene vials. Standards were prepared by drying aliquotes of standard solutions on filter paper and transfered into similar vials. Samples, standard and standard reference materials were irradiated in the rotary rack of MINT Triga Reactor with neutron flux of 10^{12} $n.cm^{-2}s^{-1}$ for about 6 hours. Irradiated samples were cooled for several days before being counted on a gamma spectrometer. Uranium was measured after 6 - 7 days cooling interval using 278 keV peak of Np^{239} isotope, while thorium was detected after 15 - 20 days cooling interval using 312 keV peak of Pa^{233} isotope. Results are calculated based on comparative method. The method was evaluated by analysing a standard reference material (IAEA-312) as follows.

The concentration of uranium and thorium in IAEA - 312 are:

Radionuclides	Our work	Recommended value
Uranium	15.8, 17.8, 17.4	16.5
Thorium	86.4, 94.2, 96.4	91.4

2.3.2 Analysis of Radium-226 and Radium-228

Samples (as received) were packed in 350 ml plastic container and analysed for radium concentration using gamma spectrometers (HPGe detectors, resolution of 2 keV at 1333 keV, analysis softwares - OXFORD's GammaTrac V1.30 and EG & G ORTEC's Gamma Vision 2.02) . Prior to analysis, the counting efficiency of gamma spectrometer was calibrated against standard, i.e. Amersham's Reference solution EW 181 containing known activities of Mn-54, Co-57, Zn-65, Y-88, Ba-133, Cs-137 and Ce-139. As samples densities were slightly different from the standards, corrections were made based on a brief study (Omar, M, *et al*, 1991). The analyses were carried out more than 20 days after packaging to allow radon gas (and its daughter radionuclides) to attain equlibrium with its parent radionuclides, Radium-226.

The photopeaks at 352 keV and 609 keV were used to calculate the activity concentration of Radium-226. As for Radium-228, it was determined through its daughter's (Ac-228, 911 keV) concentration.

3.0 Results and discussion

Table 1.0 shows the result of analysis for the oil sludge samples. All samples show very little variations of radionuclide activities, except for sample No. 2, which shows a slightly higher values of U-238 which could be attributed to experimental error.

Upon looking at the above results, the radioactivity levels of sludge samples are, technically speaking, very low i.e. lower than the normal soil samples found in Peninsular Malaysia having the average concentrations of U-238, Ra-226, Th-232 and Ra-228 found to be 73, 74, 91 and 98 Bq/kg respectively (Omar, *et al*, 1991). It is interesting to note about this result as AELB consider oil sludge is a controlled item. This has some basis, if one were to look into the oil sludge handled by oil companies that resulted from the offshore exploration whose activities ranging from 260 to 8780 Bq/kg (Yunus, 1997). Such a big difference in the radioactivity level between the samples under investigation and the one quoted above might be explained by the fact that oil sludge obtained from MSE is actually originating from oil tanker which is indeed a "clean" oil obtained after the processing of the off-shore crude above. Therefore, this low activity is expected. On the other hand, some tankers obtained and carry off-shore crude direct from the well (Abu, 1997). Under this circumstances, the low activity is therefore related to the origin of the crude having some geological history, which varies from one place to another. One such an example is North Sea crude, known to having very low activity (Abu, 1997). Thus, the analysis of oil sludge radioactivity as required by the legislation is justified at least to recognize the level and thus enabling further decisions made on the fate of the waste and the possible treatment methods henceforth undertaken.

Table 2.0 shows the radioactivity level in the filter ash. Only two samples were taken as this is only a preliminary screening analysis. Definitely, all samples show a significant increase in the radioactivity compared to the original oil sludge feed. This is expected as similar trend were reported to occur with coal combustion in power plants (Tadmor, 1986, Tso *et al*, 1996). It means that a majority of the radionuclides either dislodge from the feed samples in the form of particulates or volatalized followed by a subsequent condensation and adsorption as modelled by Lee et al (Lee, 1088a). Although the activity level is still low and comparable to most soil samples (Omar, *et al*, 1997), its enhancement effect carries a myriad of implications. One of the implications is that, the filter ash activity depends on the input activity, the higher the feed activity, the higher the activity in the filter ash.

The present study does not calculate the enhancement factor as normally reported by others (Tadmor, 1986, Tso *et al*, 1996), due to lack of data. Further quantification is therefore desireable. However, by judging from this early analysis, the radioactivity build up are in the region of 100 times or higher than the activity in the original feed. This means, for every unit input of radioactivity in the raw sludge feed, the corresponding radioactivity output in the filter ash is about 100 times more. Thus, this plant should be operated with care especially if higher activity oil sludge is fired. Consequently, for higher activity feed, a thorough safety assessment need to be made.

The second implication is the partitioning of the radionuclides. The partitioning of metals in thermal processes has been reported to be the functions of various parameters, such as the material constituent, process temperature, bed material, process dynamics, environment and time, etc. (Ho, 1993, Clifford, *et al* 1993, RCL (Canada) Ltd., 1997). One interesting observation is noted here that the Uranium nuclide tends to concentrate in the filter ash in this particular sample and process, whereas other organic sludge treatment using plasma gasifier is reportedly lodged in the slag material (RCL (Canada) Ltd. 1997). This fact is not intended to compare the two totally different technology and scenarios but is suffice to quote the various parameters that might contribute to the partitioning process. Therefore, the partitioning mechanism should be fully understood for each particular sample and plant in order to safely define the limits of the operation. Again, even upon having to understand the mechanism in general for a certain plant, the result cannot be directly applied to other non similar plant as the mechanism is very plant and process specific. It is imperative therefore to conduct studies based on specific needs.

The present study is however non conclusive with regard to the mechanism of the radionuclide partitioning, therefore further research is justified to model the partitioning process. Thus, MINT and the Universiti Kebangsaan Malaysia (UKM) are jointly pursuing this subject through few postgraduates students.

The third implication is on the safety of the plant operations. As the radionuclides settled in the filter ash and trapped in bagfilter, this filter ash is finally need to be handled during disposal. Although the activity is low, the radionuclide is of alpha-bearing type and in its dusty form can reach critical organ by means of inhalation and ingestion. Therefore, a suitable workplace protection and safety gears need to be addressed during filter ash handling.

It is a matter of interest to compare the present results with that found for coal combustion, as reported by (Tadmor, 1986). Figure 2 through 4 show the comparisons of radionuclides (U-238, Th-232 and Ra-226) in the various materials, starting from raw feed to the fly ash for both oil sludge and coal undergoing combustion process. Note that the range of radioactivity varies from sample to sample, thus for simplicity, it is represented as the minimum or maximum, as shown by sludge-low or sludge-high, etc. It is generally seen that, there is a significant and progressive enhancement of all radionuclides acitivities in the filter ash compared to the raw feed for both oil sludge and coal. For coal, the highest activity is shown in the flyash, followed by filter ash. Note that some data are not available, e.g. fly ash data for oil sludge are not measured and most filter ash data for coal are not available from the same reference above. However, generally speaking, both material exhibits similar trend, despite of different plant and process. From this simple comparisons, we can deduce and postulate that the highest enhancement effect occurs in the fly ash and followed by filter ash. As there is no data for the oil sludge fly ash and if the same phenomena as in coal applies to the oil sludge, then further investigation as to proof the above postulation is imperative, not only to satisfy the hypothesis, but more of the environmental and health impact related to the process as it has been shown that (Tadmor, 1986) this emissions at submicron levels post the highest risks.

Table 3.0 shows the result of the bed material analysis. It is seen that the radioactivity level is very low, showing that there is no accumulation of radioactivity in the bed. It is surprising as in some heavy metal bearing waste subjected fo fluidized bed incineration are reportedly retained and adsorbed in the bed material (Ho, T.C., et al 1993). Again, the contribution of the bed and sludge material compositions, temperature and time of waste in the bed material must have been playing the role. Further investigation is needed to reveal the phenomena. On the other hand, the level of radioactivity in the bed material are found to be comparable to the level found in the input sludge material, showing that the radionuclides do not settled in the bed.

4.0 CONCLUSION

The oil sludge, bed material and fly ashes were successfully analysed for radioactivity, namely U-238, Ra-226, Th-232 and Ra-228. The levels are found to be **low and comparable to common soil samples found in Peninsular Malaysia**. Some **enhancement** of the radionuclide occurs during processing but the level is still found to be relatively **low**. However, its enhancement effect has a myriad of significance and implications, which is needed to be addressed. One of the main issue is the plant feed which should be limited to the existing low activity oil sludge. For new unknown feed it shall be analyzed prior to firing with appropriate approval obtained from AELB as to the use of this new feed. Secondly, the partitioning mechanism or model should be established to understand the fundamental mechanisms that contribute to the phenomena as what has been established for coal. Analysis of fly ash radioactivity should be included in the study to proof the postulation discussed in this paper. All these activities are required to generate more data for future undertakings and actions, be it by industries or legal authorities, in oil sludge treatment using thermal treatment methods. Thus further research is therefore justified. As such the following works are being carried out by MINT - UKM:

- more sampling and analysis of oil sludge, filter ash as well as fly ash.
- laboratory studies on fluidised bed pyrolysis and combustion to model the partitioning mechanism
- co-firing of oil sludge and coal in fluidised bed combustor to study the optimum firing condition and radioactivity partioning

In whatever circumstances, the Guidelines requires the submission of the findings to the AELB for further evaluation and decision. Apart from that, the dose levels cannot be assessed as this require a full Radiological Impact Assessment (RIA) be made of which, only AELB shall decide as to the needs and relevancy. However, if the findings of radioactivity levels in the fly ash is high, it will justify the RIA studies be made to assess the health effect which could be significant as the present mitigation methods does not address this issue.

TABLE 1.0

Oil Sludge Sample

No.	Sample Code	Activity Bq/Kg.			
		U-238	Ra-226	Th-232	Ra-228
1.	No. 1	< 0.6	< 0.6	< 0.2	< 4.0
2.	No. 2	3.7 ± 0.4	< 0.6	1.0 ± 0.1	< 4.0
3.	No. 3	1.1 ± 0.1	< 0.6	0.8 ± 0.1	< 4.0
4.	No. 4	1.4 ± 0.4	< 0.6	0.7 ± 0.2	< 4.0
5.	No. 5	< 0.6	< 0.6	0.3 ± 0.1	< 4.0
6.	No. 6	< 0.6	< 0.6	< 0.2	< 4.0
7.	No. 7	< 0.6	< 0.6	0.3 ± 0.1	< 4.0
8.	No. 8	1.9 ± 0.4	< 0.6	< 0.2	< 4.0
9.	No. 9	1.8 ± 0.4	< 0.6	< 0.2	< 4.0
10.	No. 10	1.4 ± 0.4	< 0.6	< 0.2	< 4.0

TABLE 2.0

Filter Ash Sample

No.	Sample Code	Activity Bq/Kg.			
		U-238	Ra-226	Th-232	Ra-228
1.	No. 1	131 ± 6	124 ± 5	135 ± 7	150 ± 9
2.	No. 2	148 ± 8	112 ± 8	154 ± 4	150 ± 12

TABLE 3.0

Bed Material Sample

No.	Sample Code	Activity Bq/Kg.			
		U- 238	Ra-226	Th-232	Ra-228
1.	No. 1	3.5 ± 0.2	< 6.0	1.0 ± 0.1	< 4.0
2.	No. 2	2.6 ± 0.4	< 6.0	0.4 ± 0.1	< 4.0

Acknowledgements

The authors would like to thanks Mr Fuad Abu (AELB), Dr Nahrul Khair A. Rashid (MINT), Techno Indah/MSE, UKM, and other MINT staff involved in this project for their invaluable contributions.

References:

1. Omar M, (1995), The effect of sample matrix density on counting efficiency, unpublished data.

2. David Oven, (1996), personal communication with Yunus, M.N.M, MINT,.

3. Lee, C.C. (1988), A model analysis of metal partitioning. JAPCA, 38: 941-945.

4. Omar, M, Ibrahim, M.Y., Hassan, A., Mahmood, C.S., Lau, H.M., Ahmad, Z., Sharifuddin, M.A., (1991), Environmental Radiation and Radioactivity Levels in Malaysia, Proc. IRPA National Seminar, Strategic Sector, Penang, Malaysia.

5. Ho, T.C., Chu, H.W., Hopper, J.R. (1993), Metal volatilisation and separation during incineration, Waste Management, Vol. 13, pp 455-466.

6. Clifford, D.A., Chen, S.S. and Reznik, C. (1993), Volatilizing toxic metals from soil Waste Management, Vol. 13, pp467-479.

7. Resoption Canada Ltd. (1997), Personal Correspondence with Yunus, M.M.M, MINT.

8. Abu, M.F. (1997), personal communication with Yunus, M.M.N.

9. Yunus, M.N.M. *et al*, (1997), Proposed NORM waste Management Facility for PETRONAS, MINT classified internal report to Enhance Plasma Venture Sdn. Bhd, Malaysia.

10. Tadmor, J, (1986), Radioactivity From Coal-Fired Power Plants: A Review J. Environ. Radioactivity, 4, pp 177-204.

11. W.Tso, M - Y & Leung, J.K.C. (1996), Radiological Impact of Coal Ash from the Power Plants in Hong Kong, J. Environ. Radioactivity, 30, pp 1-14.

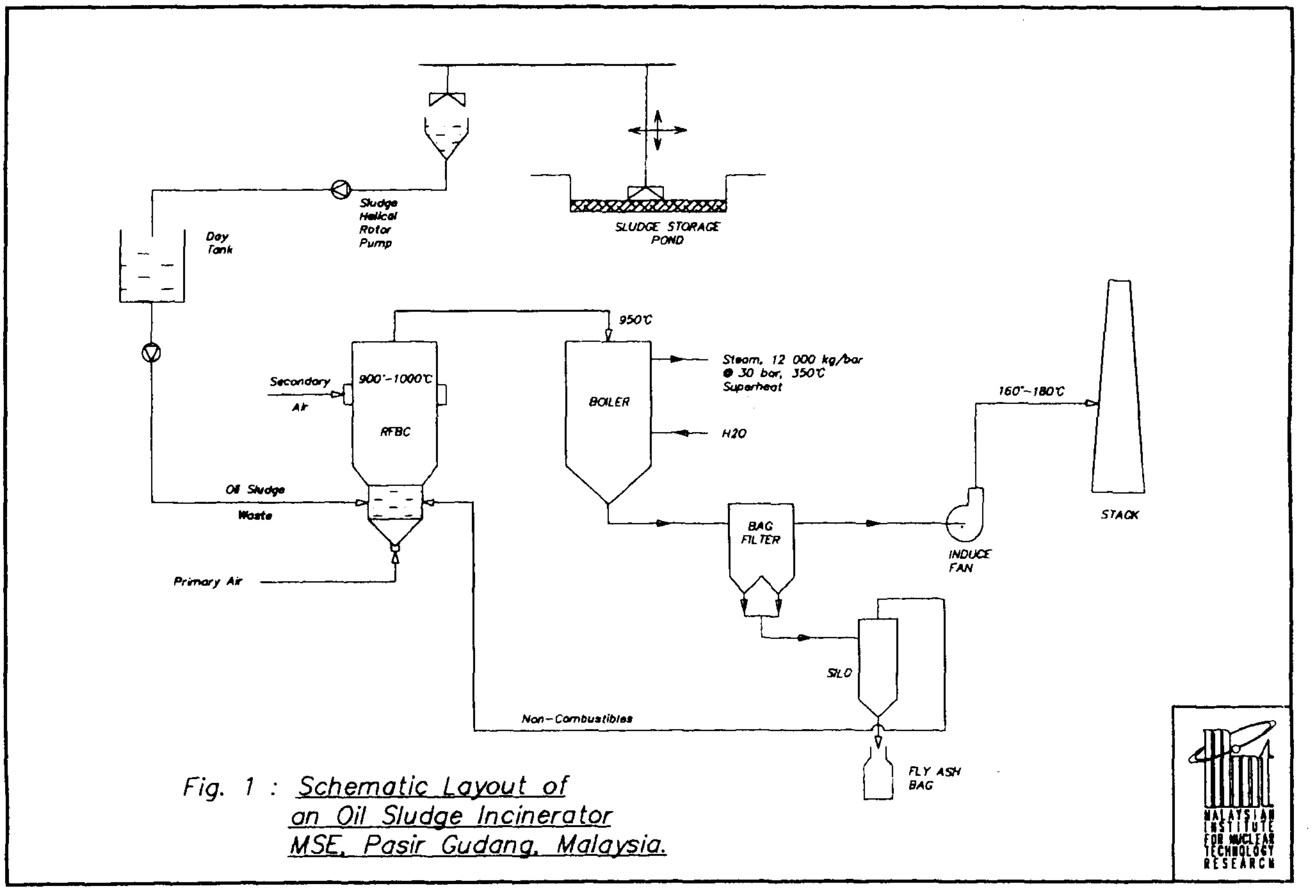

Fig. 1 : Schematic Layout of an Oil Sludge Incinerator MSE, Pasir Gudang, Malaysia.

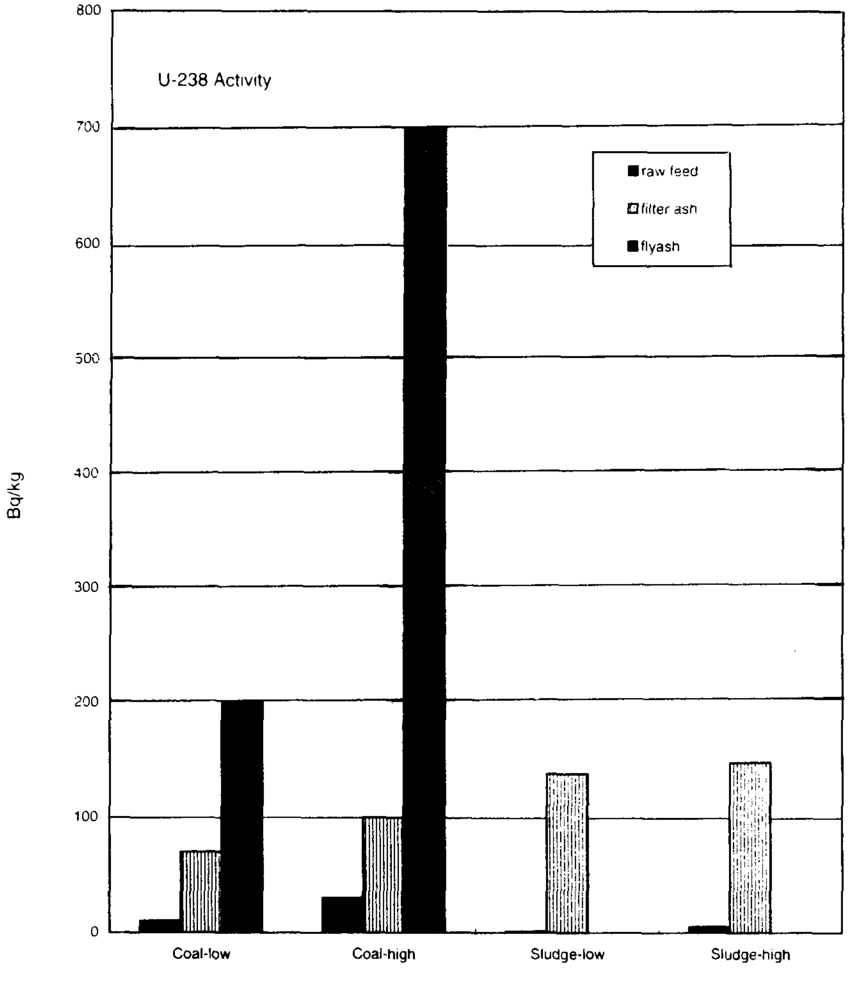

Figure 2: Comparison between coal and oil sludge U-238 activity partitioning
(coal data due to Tadmor,1986)

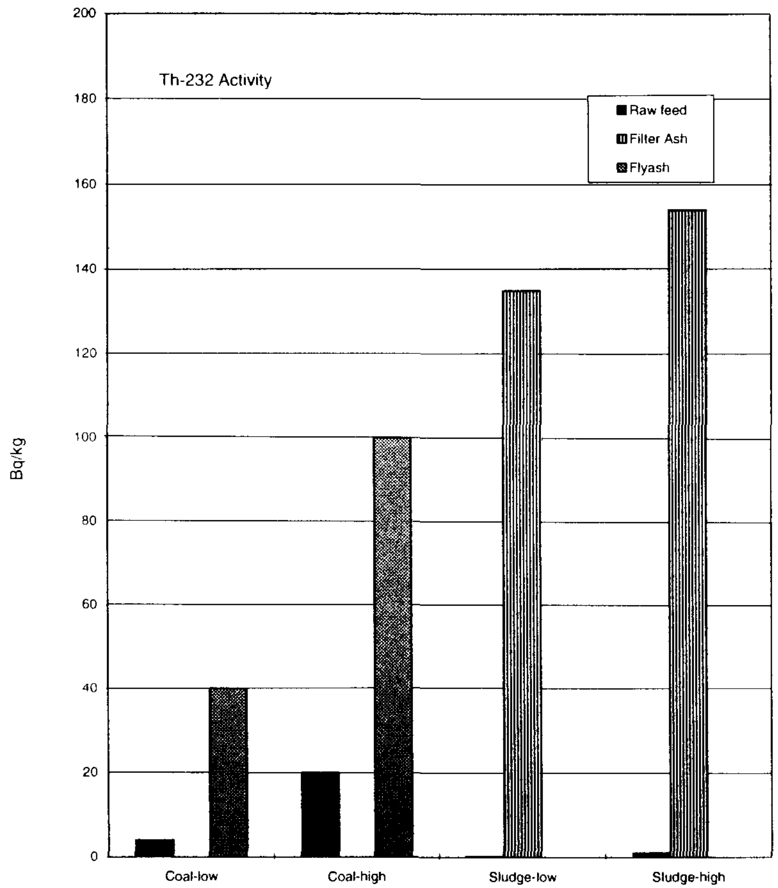

Figure 3: Comparison between coal and oil sludge Th-232 activity partitioning (coal data due to Tadmore.1986)

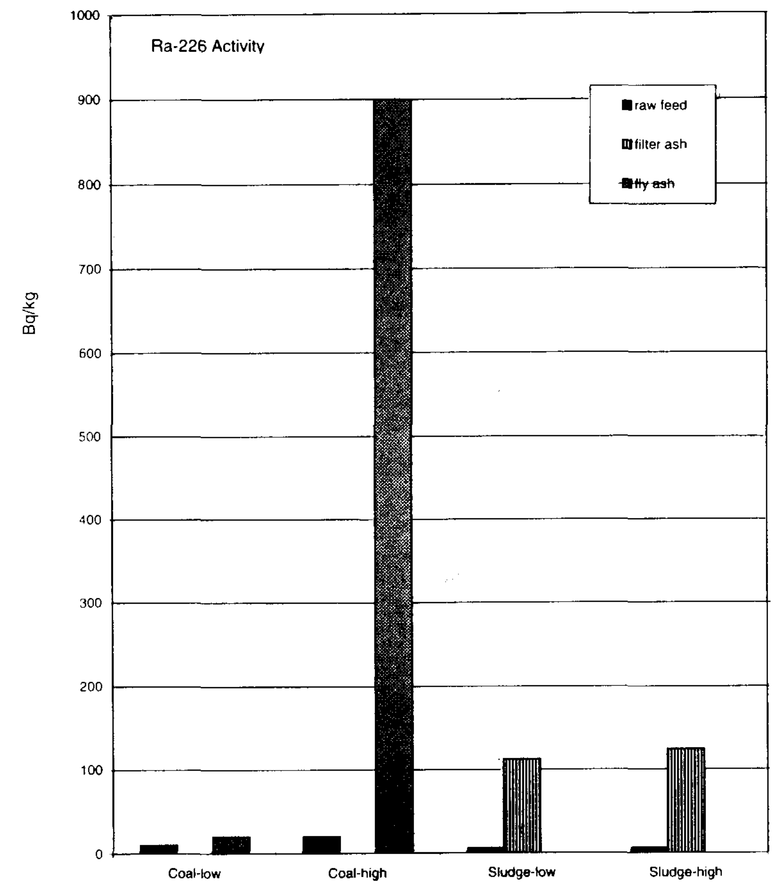

Figure 4: Comparison between coal and sludge Ra-226 activity partitioning *(coal data due to Tadmore, 1986)*