Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Sonar, N. L. , Sonavane, M. S. , Valsala, T. P. , Kulkarni, Y. , Raj, Kanwar and Manchanda, V. K.(2009) 'Use of Nickel Sulphide-PMMA Composite Beads for Removal of ^{106}Ru from Alkaline Radioactive Liquid Waste', Separation Science and Technology, 44: 15, 3753 — 3769

To link to this Article: DOI: 10.1080/01496390903182529

URL: http://dx.doi.org/10.1080/01496390903182529

Separation Science and Technology, 44: 3753–3769, 2009
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903182529

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Use of Nickel Sulphide–PMMA Composite Beads for Removal of ^{106}Ru from Alkaline Radioactive Liquid Waste

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Abstract: Use of NiS coprecipitation was found to be very effective at a concentration level of 2500 ppm of Ni^{+2} and 1300 ppm of S^{-2} for the effective removal of ^{106}Ru from the effluent stream. However, the NiS precipitate increases the sludge volume. Efforts were made to form the composite material of NiS in combination with Poly methyl metha acrylate (PMMA) polymer beads. The NiS–PMMA composite beads were loaded in a column and its ruthenium uptake behavior was studied. The NiS–PMMA beads were found to be functioning satisfactorily in alkaline conditions. It has shown a K_d value of about 8000–9000. The NiS–PMMA composite material has also shown the potential for the uptake of ^{125}Sb. The effect of salt concentration on the K_d value is negligible. The equilibrium conditions are achieved in around 25–30 min in batch mode of operation. The composite material can be suitably used in the column mode of operation.

Keywords: ion exchange, nickel sulphide, polymethyl metha acrylates, resorcinol formaldehyde (RF) resin, ruthenium

Received 20 November 2008; accepted 12 May 2009.

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INTRODUCTION

^{106}Ru is one of the radionuclides obtained as a fission product with a fission yield of about 0.4%. The chemistry of ruthenium is very complicated. It has many oxidation states from 0–VIII and forms a large number of nitrosyl complexes like $RuNO(NO_3)_3(H_2O)_2$; $RuNO(NO_3)_2(OH)(H_2O)_2$ etc (1–4). This makes it a troublesome nuclide amongst the fission products.

In acidic waste stream Ru exist as a complex species of the nitrosyl ruthenium (Ru-NO) group (1–3). This can be represented by a general formula (5).

$$[Ru(NO)(NO_3)_x(NO_2)_y(OH)_z(H_2O)_{5-x-y-z}]^{3-x-y-z}$$

With the number and type of ligand attached to the RuNO group, the complex can be cationic, neutral, or anionic. It may exist as ruthenate ion (RuO_4^{-2}) or perruthenate ion (RuO_4) in alkaline solution (6). When the acidic waste is neutralized and made alkaline, the nature of the ruthenium species in alkaline condition is different. In such a solution it may exist as $RuNO(OH)_3 \cdot H_2O$ (7).

Reprocessing of the spent fuel from the reactor generates broadly two categories of radioactive liquid waste stream viz high level liquid waste (HLW) and intermediate level radioactive liquid waste (ILW). HLW in acidic condition is stored in stainless steel tanks for its subsequent treatments viz actinide partitioning (8,9) or vitrification (10,11). The waste is concentrated prior to its storage for volume reduction. During the concentration process of HLW, the condensate stream generated is acidic and ILW in nature. Second cycle raffinate generated during the reprocessing of the spent fuel is another source of the ILW. This waste at the source is acidic in nature. The acidic ILW is neutralized prior to storage in a carbon steel tank. Major radionuclides present in the waste are ^{137}Cs, ^{90}Sr, ^{106}Ru, and trace concentration of actinides. This neutralized waste is taken up for ^{137}Cs removal using a specific resorcinol formaldehyde ion exchange resin.

Prior to the ion exchange treatment, major proportions of strontium and alpha radionuclides present in ILW are removed by alkaline precipitation. The resultant supernatant solution contains ^{137}Cs, ^{134}Cs, and ^{106}Ru as major radionuclides. It is passed through the RF resin column to specifically remove ^{137}Cs and ^{134}Cs from the waste (12). However, the RF resin does not provide any decontamination for ^{106}Ru and which reports in the column effluent. Thus the radioactive effluent stream of the ion exchange treatment process, which is low active in nature, needs chemical treatment for the removal of residual ^{137}Cs, ^{90}Sr, and ^{106}Ru. Since the conventional chemical treatment process does not give any DF for Ru, specific chemical treatment is required for Ru removal prior to discharge the column effluent in alkaline condition.

A wide variety of sorbents are reported in the literature for the uptake of radioruthenium from various radioactive waste streams. ^{106}Ru can be removed from such waste streams by using Fe^{2+} as carrier in reducing atmosphere (13,15). However, this method provides poor decontamination factor of about 5–8, which is not adequate for the effective removal of ^{106}Ru. Use of Zinc charcoal mixture as adsorbent has also been explored for the removal of ^{106}Ru from the radioactive waste stream (13–16). This method was found to be useful in acidic conditions at pH 2.0 and provides an overall decontamination of about 10 (upto loading of 100 bed volume of such waste) which was not sufficient for the effective removal of ^{106}Ru from the present waste stream. Polyaniline has also been used for the removal of ^{106}Ru from aqueous waste stream at pH 5.0 and above (17–19). The adsorption of Ru–chloro, Ru-NH_3, and Ru-EDTA complexes on polysulfur nitride material is also reported (20). Ruthenium in nitric acid solution can be oxidized by the addition of cerric nitrate to RuO_4 which can be further extracted in n-paraffin oil (21). Electrolytic oxidation of ruthenium has also been reported (22). Use of copper ferrocyanide formed with sodium ferrocyanide and copper sulphate was also reported for the removal of ^{106}Ru from the radioactive liquid waste stream at pH 4–6 (23).

Use of CuS insitu coprecipitation for ^{106}Ru decontamination from waste has also been reported. However, the method works at pH 1.0. However, this method has given limitation of H_2S gas formation in acidic region and poor DF value (24). On the other hand, the effective removal of ^{106}Ru was achieved with alkaline in situ precipitation of NiS (25,26).

An earlier study of the co-precipitation of Ru with in situ precipitation of NiS gave very good decontamination with respect to Ru. Concentration of 2500 ppm as Ni^{2+} and 1326 ppm as S^{2-} is optimum to give maximum decontamination with respect to ^{106}Ru (25,26) with a decontamination factor of about 60–250 using multiple step precipitation. However, efforts were made to convert the NiS into a spherical bead form by adsorbing it on a suitable substrate so as to use it effectively in column mode operation. A composite material was made by using NiS powder and Polymethyl metha acrylate (PMMA) beads. Detailed studies were carried out to evaluate the performance of the NiS–PMMA beads. The effects of different parameters such as salt concentration, pH, and time on the uptake behavior were evaluated and the capacity of the NiS powder material was studied.

EXPERIMENTAL

All reagents used in this study were of AR grade.

Preparation of NiS–PMMA Composite Beads

NiS precipitate was prepared by a conventional method by mixing Nickel Nitrate with Sodium Sulphide in stoichiometric proportion at pH 12.0. The precipitate was washed thoroughly with distilled water to remove unreacted chemicals as well as excess alkali and finally dried. The NiS powder thus obtained was characterized by X-ray difractometer (XRD, Fig. 1) and Scanning electron microscope (SEM, Fig. 2). The instrument used is Philips ESEM, Model–XL30 coupled with EDAX.

The NiS–PMMA composite material was prepared as reported earlier (27). The NiS–PMMA composite beads with NiS content varying from 10–50% (wt/wt) were prepared by mixing the NiS powder and PMMA beads in the presence of a binder methyl metha acrylate monomer. These composite beads were finally dried at ~50°C in the oven.

Preparation of Condensate Waste

The actual radioactive condensate waste obtained from vitrification operation is acidic in nature. During ion exchange treatment process

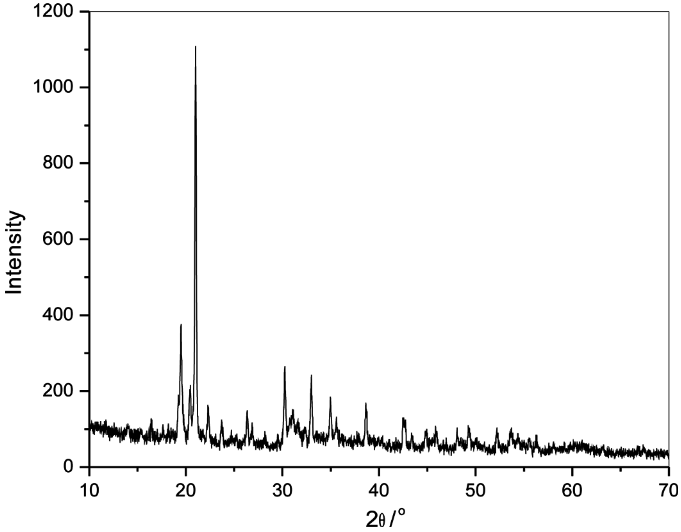

Figure 1. XRD pattern of Nickel Sulfide Powder.

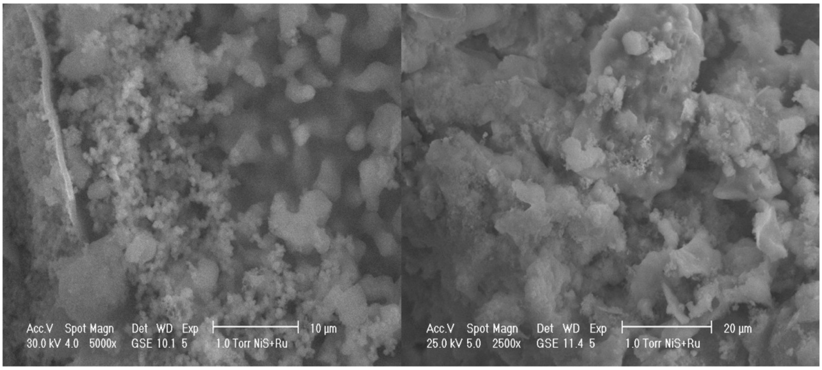

Figure 2. SEM Photograph of NiS powder.

for removal of $^{134+137}$Cs, the waste is made alkaline and then passed through RF resin column. However, for present work, $^{134+137}$Cs from acidic waste were removed by treatment with Ammonium molybdo phosphate (AMP). The resultant solution was made alkaline upto pH 11 and taken up for further experimental study. The properties of the waste are listed in Table 1.

i. K_d value Evaluation

0.1 gm of the sorbent material prepared above was equilibrated with 10 ml of the condensate waste for one hour. The initial and final activity of ^{106}Ru was monitored using the HPGe detector based 8 K multichannel analyser. The K_d value was calculated as follows.

$$Kd = \frac{C_i - C_f}{C_f} \; x \frac{V}{W} \quad (ml/gm) \tag{1}$$

Where, C_i and C_f are the initial and final concentrations of ^{106}Ru

Table 1. Properties of the synthetic alkaline radioactive liquid waste

Sr. No.	Properties	value
1	pH	11.0
2	Total solids, % (wt/vol)	3.0
3	Gross beta, mCi/L	2.0
4	Cs^{137}, mCi/L	2.7×10^{-4}
5	Ru^{106}, mCi/L	3.13×10^{-3}
6	Sb^{125}, mCi/L	5.81×10^{-3}

V is the volume (ml) of waste
W is weight(g) of the composite material.

ii. Effect of pH
In order to understand the effect of pH on K_d value of Ru on NiS–PMMA material, the experiments were conducted by varying the pH of the solution from 1 to 11. The pH and Kd value obtained are listed in Fig. 3.

iii. Effect of salt concentration
During the neutralization of the acidic waste, a large amount of salt gets introduced into the waste. Hence experiments were performed to understand the effect of salt concentration on the K_d value of the NiS–PMMA composite beads. Salt in the form of sodium nitrate was added to the waste. Salt concentration was varied from 3% to 28%. The concentration of salt and Kd value obtained is listed in Fig. 4.

iv. Effect of NiS: PMMA composition
The K_d values of NiS–PMMA composite material with different composition were also evaluated. The results are presented in Fig. 5.

v. Effect of time period on uptake behavior of NiS–PMMA composite material
In order to know the uptake behavior of NiS–PMMA composite material for ^{106}Ru with respect to time, the NiS–PMMA(30%) composite material was equilibrated with ^{106}Ru solution at pH 11.0 for different time interval. The removal of ruthenium from

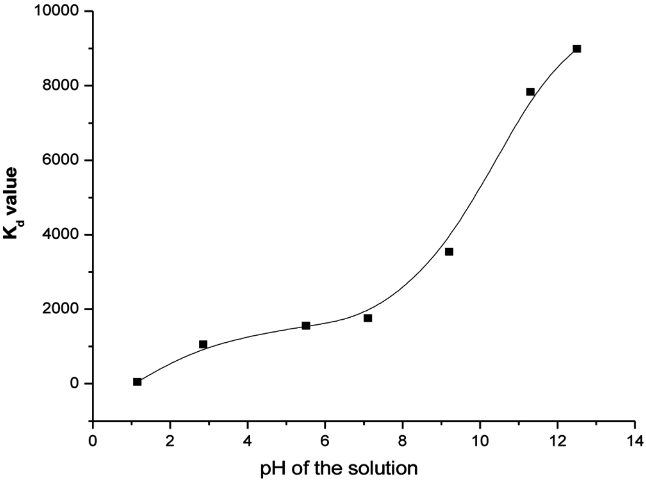

Figure 3. Effect of pH on Kd value of NiS PMMA composite material.

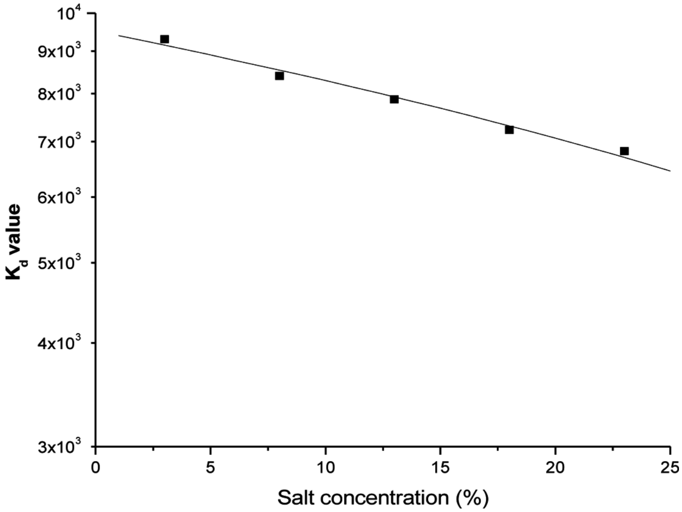

Figure 4. Effect of salt concentration on K_d value.

the liquid stream was plotted as a fraction of ruthenium left in solution as a function of time as shown in Fig. 6.

vi. Sorption capacity of the NiS powder

In order to see the ion exchange capacity of the NiS powder, the

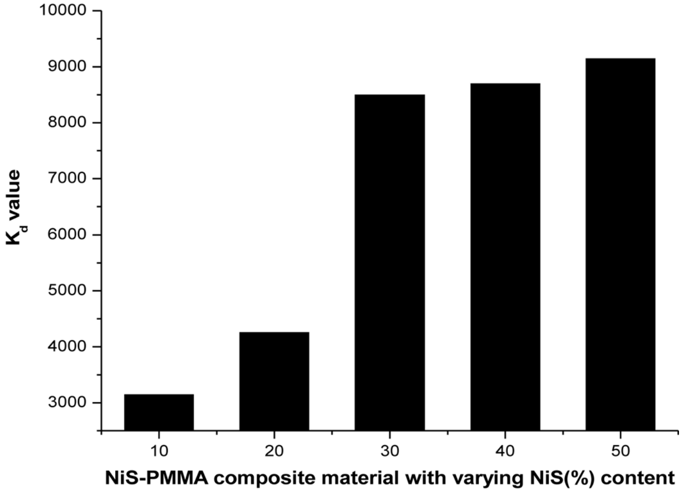

Figure 5. Kd Vs different NiS–PMMA composite materials.

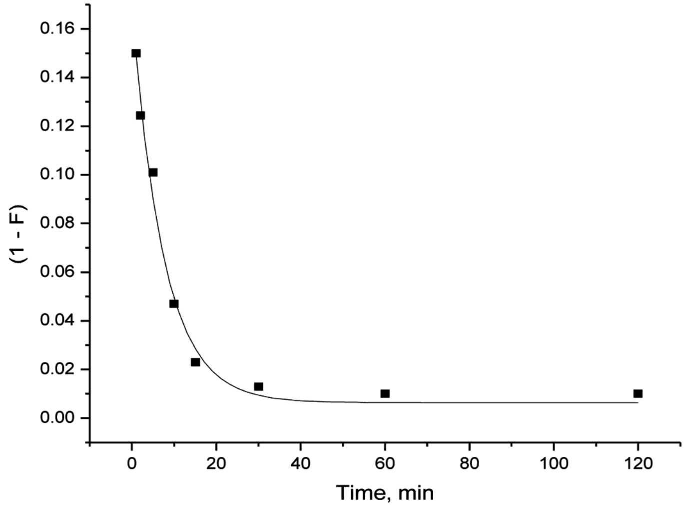

Figure 6. Kinetics for sorption of ^{106}Ru on NiS–PMMA composite material.

dried powder obtained by NiS precipitation was equilibrated with the solution of inactive ruthenium of 25 ppm spiked with ^{106}Ru for a period of five hours. The solid–liquid phase was separated by centrifugation. The activity was monitored after equilibration and its ion exchange capacity was evaluated.

vii. Adsorption behavior of ^{125}Sb on NiS–PMMA composite material
The condensate waste used for the study was also having radioactive isotope ^{125}Sb. The NiS–PMMA composite material has shown the potential for the uptake of ^{125}Sb. Hence its adsorption behavior with NiS–PMMA composite material was studied. The Kd value of ^{125}Sb for the NiS–PMMA composite material (30%) was evaluated and effect of salt concentration on K_d value was also studied. The results are presented in Table 2.

Table 2. Effect of salt concentration on Kd value of NiS–PMMA composite material for ^{125}Sb

Sr. No.	Total solid % (wt/vol)	Kd value
1	3	2494
2	8	2565
3	13	2958
4	18	3317
5	23	2805

viii. Column performance evaluation of NiS–PMMA composite material

Preparation of Simulated Waste for Column Study

Simulated waste was prepared for the column study by taking inactive ruthenium equivalent to 1.35 mCi/L. Salt content was adjusted to 5% by sodium nitrate and pH was adjusted to 11.0. The solution was spiked with ^{106}Ru having activity content 1.52×10^{-3} mCi/L for radiometric ease of measurement. This waste was used as feed to the column.

Column operation

The glass burette of 10 ml capacity was used as a column. The burette was filled upto 1.6 ml (weight:1 gm) with composite NiS–PMMA (30%) beads. The beads are having a particle size ranging from 0.4–0.7 mm diameter. The details of the column are given in Table 3. The synthetic waste prepared above was passed through the column with a flow rate of 5 bed volume per hour. Total 2200 bed volume of the waste was passed through the column. The column effluent samples were collected periodically and monitored for ^{106}Ru activity content. The performance of the column is shown in Fig. 7.

ix. Effect of temperature

In order to understand the effect of temperature on the sorption behavior of ruthenium on the composite material, ruthenium solution was equilibrated with the composite material at varied temperature. The effect of temperature on the equilibrium constant is given in Fig. 8.

x. Effect of Ni : S ratio during precipitation

NiS prepared using stoichiometric proportion of nickel nitrate and sodium sulphide was used for all other experiments. However, to

Table 3. Details of the NiS–PMMA column

Column material	NiS-PMMA composite material
Column	10 ml glass burette
Bed volume	1.6 ml
Weight	1.0 gm
Bed height	2.0 cm
Bed diameter	0.6 cm
Flow rate	4–5 bed volume/hour 6.5–8.0 ml/hour
Total volume of waste passed	3520 ml (2200 BV)

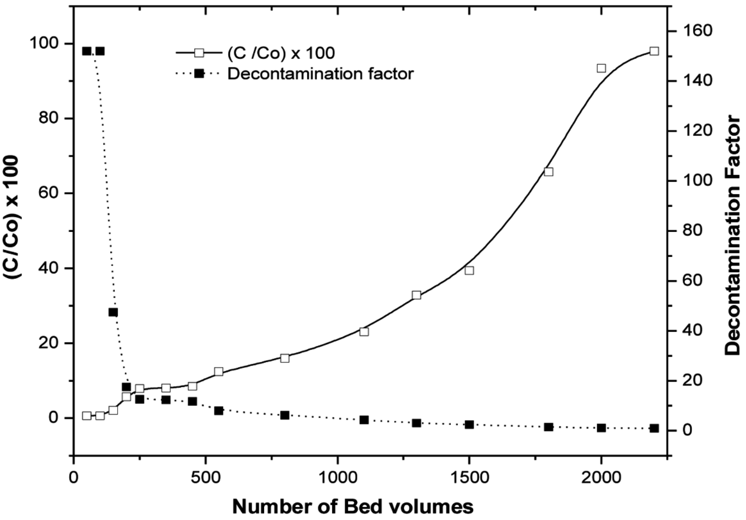

Figure 7. Performance of the NiS–PMMA column.

see the effect of molar ratio, experiments were performed by preparing nickel sulphide with varying molar ratio of $Ni^{+2} : S^{-2}$. The molar ratio was varied from 1 : 0.8 to 1 : 1.25. The NiS thus obtained was

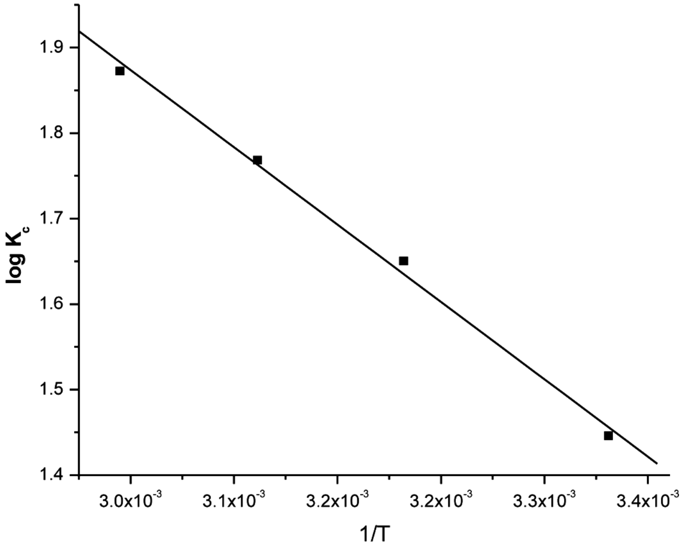

Figure 8. Influence of temperature on sorption of Ru on NiS-PMMA composite material.

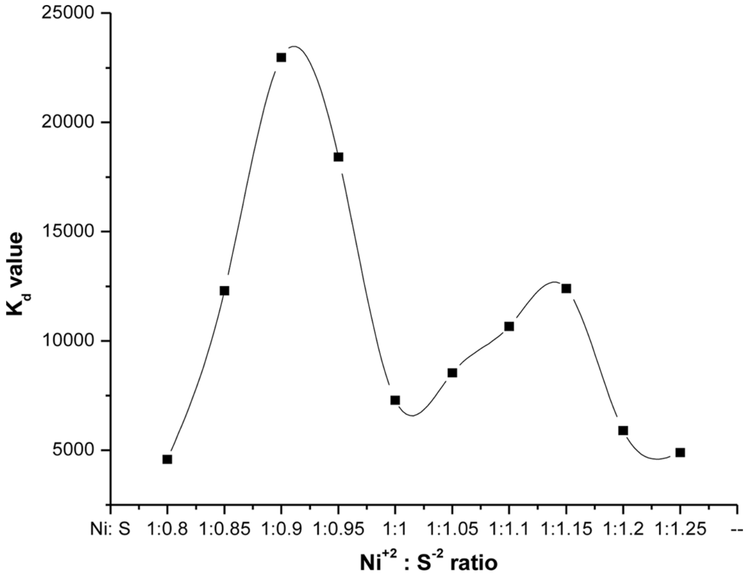

Figure 9. Effect of $Ni^{+2}:S^{-2}$ molar ratio on Kd value of ^{106}Ru.

taken up for its K_d value evaluation with respect to ^{106}Ru. The detail is shown in Fig. 9.

All the experiments were performed in triplicate and the average results are discussed.

RESULT AND DISCUSSION

Physical Characterization

The XRD pattern of the synthesized NiS powder is shown in Fig. 1. All the peaks can be indexed to hexagonal phase NiS with lattice parameters a = 3.416A, c = 5.23, which are consistent with the reported data (a = 3.420A, c = 5.300A, JCPDS Card No. 75–0613). The SEM photographs (Fig. 2) obtained shows that the particle size is varying between 20–30 μm.

K_d Value

The K_d value was found to be 8500–9000 ml/gm for the condensate waste with NiS–PMMA (30%) beads. The NiS–PMMA composite material was found to be performing better in alkaline condition (Fig. 3), since NiS precipitation takes place in alkaline condition (28). In acidic condition the lower K_d value can be explained due to the dissolution of the NiS precipitate in acidic media.

With increase in salt concentration, the K_d value is decreasing marginally (Fig. 4) indicating that the K_d value is not getting affected by an increase in the total solid content in the liquid stream.

As seen from Fig. 5, the K_d value varies from 3000–9000 ml/gm for the NiS–PMMA composite beads having an NiS content varying from 10%–50%. The K_d value was found to be increasing upto 30% NiS-PMMA material. Further increase in the NiS content, the Kd value increases marginally. This indicates that above 30% concentration, there must be a formation of a multilayer over the PMMA beads.

Column Performance

For the synthetic radioactive waste having ^{106}Ru activity of the order of 1.35 mCi/L, after 200 bed volume 2% leakage of Ru activity has been observed. Initially a DF of 150 was observed upto 100 bed volume which decreased to 20 at 200 bed volumes and after 250 bed volumes, a decontamination factor of about 10 is observed. As shown in Fig. 7, total 2200 bed volumes of the waste was required to saturate the column. Column study has indicated that the composite NiS–PMMA beads can be used efficiently for removal of ^{106}Ru from the alkaline waste stream.

The sorption capacity of the NiS powder was found to be 0.05 mmole/gm.

The NiS–PMMA composite material has shown potential for uptake of ^{125}Sb from the waste solution. The K_d value of ^{125}Sb for 30% NiS–PMMA composite material was found to be in the range of 2500–3000. From Table 2, it is observed that the K_d value is not getting affected by salt concentration.

Sorption Kinetics Study

The rate of transfer of ions from aqueous phase to NiS–PMMA composite material was studied by equilibrating the NiS–PMMA composite material (10%) with the ^{106}Ru solution for a different length of time. The phase adsorption kinetics was monitored in terms of fractional attainment of equilibrium expressed by (29).

$$F = \frac{[M]_t}{[M]_{eq}} \tag{2}$$

where $[M]_t$ and $[M]_{eq}$ are the concentration of ^{106}Ru on solid phase at time 't' and that at equilibrium respectively.

The kinetic data were plotted in terms of (1−F) values as a function of equilibration time and is shown in Fig. 6. From this figure, it is evident that the equilibration condition reached within 25–30 minutes.

Thermodynamic Studies

The influence of temperature variation was examined on the sorption of ruthenium at the temperature 25, 40, 50, and 60°C. The plot of log K_c versus 1/T is shown in Fig. 8. The value of K_c, the equilibrium constant can be worked at each temperature using the following relationship,

$$K_c = \frac{F_e}{1 - F_e} \tag{3}$$

where, F_e is the fraction sorbed at equilibrium and is given by

$$F_e = \frac{A_i - A_f}{A_i} \tag{4}$$

where A_i and A_f are initial and final concentration of the adsorbing species.

The equations given below may be used to evaluate the values of ΔG, ΔH, and ΔS.

$$\Delta G = -RT \ln K_c \tag{5}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\therefore -2.303\ RT \log K_c = \Delta H - T\ \Delta S$$

$$\log Kc = \frac{-\Delta H}{2.393RT} + \frac{\Delta S}{2.303R} \tag{6}$$

From the slope and intercept of the plot in Fig. 8, the values ΔH and ΔS were computed and from Eq. (5) ΔG, are computed as given in Table 4.

Sorption Mechanism

The sorption of ruthenium ions increases with increase in temperature, which indicates the strengthening of the adsorbate–adsorbent interaction

Table 4. Thermodynamic parameters

Temperature (K)	ΔG (kJ/mmol)	ΔH (kJ/mmol)	ΔS (J/mol.K)
300	−8.305	10.731	110.25
313	−9.891		
323	−10.936		
333	−11.939		

at high temperature. The increase in adsorption with temperature suggested that the active surface centers for sorption increase with temperature. Another reason may be due to the change in pore size and enhanced rate of intraparticle diffusion of solute as diffusion is an endothermic process. It is evident from Table 4 that the value of ΔG is negative indicating the spontaneous nature of sorption. The value of ΔH is positive indicating the endothermic nature of sorption. The possible explanation is that in order to adsorb the ions, they are to some extent dehydrated, which requires energy (30). The removal of water from ions is essentially an endothermic process and it appears that the endothermicity of the desolvation process exceeds the heat of adsorption. The lowering in the ΔG value with increasing temperature shows that the adsorption of ions on NiS–PMMA composite material surface becomes favorable at high temperature. Since the adsorption is endothermic, the adsorption process is therefore made spontaneous because of positive entropy changes.

The sorption may be interpreted in terms of the solvation type bond formation between the ruthenium species and solid NiS–PMMA composite material surface based on ionic bonding comprising ion-exchange or ion-associated interaction (31). This has been supported by the experimental finding that when NiS was prepared with a different mole ratio of $Ni^{+2}:S^{-2}$, NiS with 1 : 1 mole ratio has shown a lower K_d value as shown in Fig. 9. NiS with higher Ni^{+2} moles has shown higher K_d value as compare to NiS with higher S^{-2} moles. In case of NiS with higher Ni^{+2} moles, the excess of Ni^{+2} ions are getting adsorbed on the surface of the precipitate, which provides ion associated interaction with the anionic species of ruthenium from the alkaline solution.

CONCLUSION

The NiS–PMMA composite material has very good K_d value with respect to ^{106}Ru. The composite material is working satisfactorily in alkaline condition. The effect of the salt concentration on the K_d value of the composite material is negligible. 30% of the NiS loading on PMMA beads is optimum for effective removal of ^{106}Ru from alkaline radioactive liquid waste. Further increase in the NiS content has not given any additional advantage. The column studies have indicated an initial DF of 150 upto 100 bed volumes which gradually decreased to 10 at 450 bed volumes, which is far better than that of chemical precipitation. More than 95% of ^{106}Ru can be removed within a time period of 25–30 minutes. Based on these findings, it is concluded that the NiS–PMMA composite material can be used for the effective removal of ^{106}Ru in the column mode. This in effect decreases the secondary waste generation in the form of chemical sludge. The sorption of ^{106}Ru on the composite material is a spontaneous and endothermic reaction and follows ion associated interaction. The NiS–PMMA composite material also has the potential for the uptake of ^{125}Sb from the radioactive liquid waste.

ACKNOWLEDGEMENT

The authors extend their gratitude towards Shri. R.K. Mishra and Dr. J.G. Shah for providing analytical support for the physical characterization of the NiS powder material using XRD and SEM techniques. Authors are also thankful to Shri. R. D. Changrani, Chief Superintendent, NRGF (T), for his guidance and interest in the work.

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