

# Uptake of Ruthenium Bearing Waste by Co-Precipitation using Lead Sulfide as Scavenger

Ajay Kumar Mishra, B S Panigrahi



**Abstract:** During the fission of Uranium for generating electricity, fission products are produced. Ru-106 is one among them. In the decontamination of nuclear components using decontaminating agents like EDTA, NDA, oxalic acid etc, Ruthenium gets complexed and the waste generated as liquid contains Ru-106 in the complex state. It is necessary to free Ru-106 from the complex by oxidation of the complex. This will generate Ruthenium effluent with Ru-106 in the free state amenable for further treatment. An attempt has been made to co precipitate Ruthenium along with lead sulphide. The optimum pH, dosing of chemicals needed for in situ precipitation of lead sulphide were estimated in the batch study. Column studies using lead sulphide on polyurethane foam as column material were carried out for the treatment of Ruthenium bearing effluent. The optimum flow rate for maximum removal of Ruthenium was found to be 20 BV/h. Under optimized condition the max removal of Ruthenium was found to be 84% in the batch study, and 80% in the column study.

**Keywords:** Zeta Potential, Co Precipitation, Decontamination, Treatment

## I. INTRODUCTION

Thick film chip resistors make use of Ruthenium dioxide, lead and bismuth ruthenates. [1],[2] Also they are used in electrolytic cells for chemical processes such as generating chlorine from salt water [3]. Ru may be useful in the removal of H<sub>2</sub>S in oil refineries and other industrial processing facilities [4]. In the organic and pharmaceutical chemistry [5] Organometallic ruthenium carbene have been found to be highly efficient catalysts for olefin metathesis. Also they are used in dye-sensitized solar cells. Uptake of Ru from the Ru bearing effluent in the decontaminated effluent enables easier further treatment of the effluent. Ru exists in multiple valence states both in cationic and anionic forms, In our experiment ruthenium trichloride has been used for treatment for inactive studies. Literatures shows treatment of ruthenium by adsorption by ferrous, nickel, cobalt and manganese sulphides [6]. In the present study we have taken up co precipitation of Ru-106 along with lead sulphide.

## 1.1 Materials and Methods

The study used chemicals, which were AR grade. Ruthenium trichloride, Lead nitrate and sodium sulphide procured from M/s. Banci chemicals, Chennai, were used for the experiment. the lead sulphide was coated over polyurethane foam procured from E. Merck. Ethyl alcohol and acetone were used as solvents and polyvinyl acetate employed as binder (column material) for the column studies on the treatment of ruthenium effluent were procured from M/s Novkar chemicals, Chennai.

## II. EXPERIMENTAL

### 2.1 Measurement of Settling Nature of the Sulphides

The precipitated lead sulphide and Ruthenium sulphide were suspended in DM water whose pH was adjusted to pH=1 to 8 using HCl and NaOH respectively. The zeta potential in each case was estimated. Particle size at each pH was estimated. Figure 1. Shows the Variation of Zeta potential lead Sulphide and Ruthenium sulphide as function of pH.

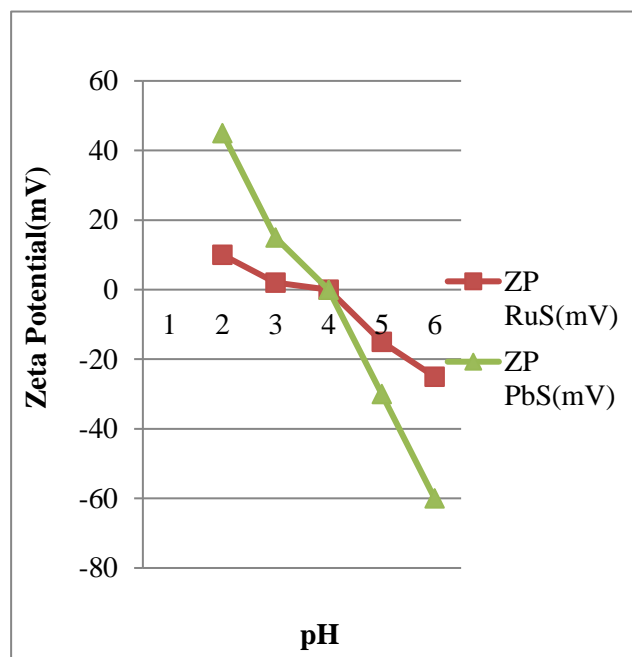


Fig. 1. Variation of Zeta potential lead Sulphide and Ruthenium sulphide as function of pH

Figure 2 Shows particle size of lead Sulphide and Ruthenium sulphide as function of pH.

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# Uptake Of Ruthenium Bearing Waste by Co-Precipitation using Lead Sulphide as Scavenger

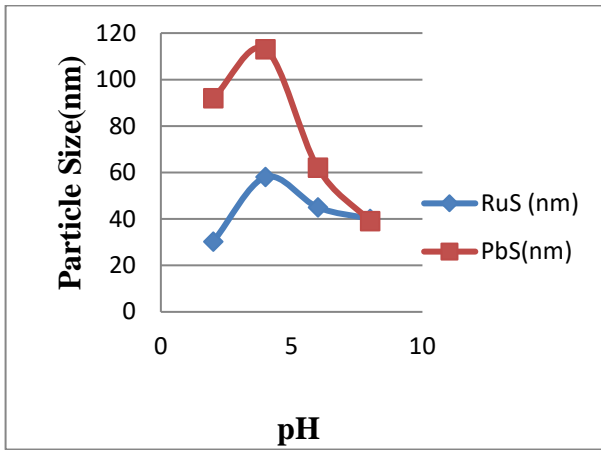


Fig. 2. Variation of Particle size of Ruthenium Sulphide and Lead Sulphide as function of Ph

## 2.2 Optimisation of pH of Treatment of Ruthenium Effluent

It is necessary to optimize the pH of the effluent for the co precipitation of Ruthenium. Five different beakers each containing 100 ml of 100 ppm Ruthenium at different pH from 2 to 8. They were treated with 36 ppm of lead nitrate and 8.5 ppm of sodium sulphide, which corresponds to 110% stoichiometry of the chemical reaction between lead nitrate and sodium sulphide. The percentage removal of Ruthenium as function of pH is shown in fig.3

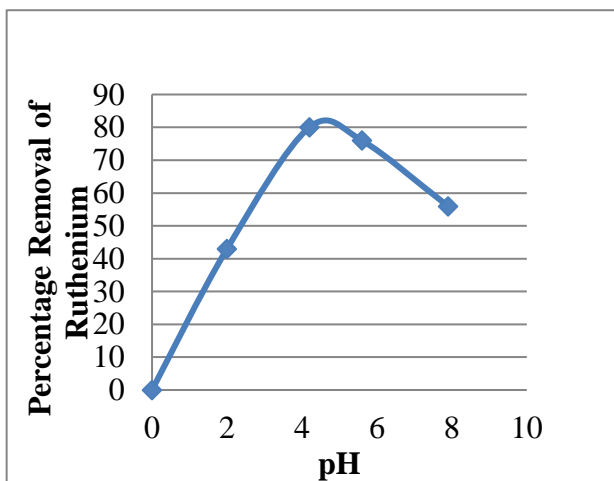


Fig. 3. Percentage Removal of Ruthenium as function of pH

## 2.3 Optimisation of dosing of sulphides

Since larger amount of lead sulphides during the coprecipitation of Ruthenium may aid in the better removal of Ruthenium, it is imperative to optimize the dosing for the precipitation of lead sulphide. 100 ml of 100 ppm Ruthenium as  $RuCl_3$  solution in DM water at pH= 4.2 in water were taken in three different beakers and were treated with 33,36 and 43 ppm of lead nitrate and 7.8, 8.5 and 10.1 ppm of sodium sulphide separately. The dosing of these chemicals correspond to 100, 110 and 120 % stoichiometry of the chemical reactions between lead nitrate and sodium sulphide giving rise to lead sulphide.  $Ru^{106}$  in the supernatant was analysed as function of Percentage stoichiometry of the reaction producing lead sulphide used as carrier for Ruthenium. Figure 4 shows Percentage removal of ruthenium as function of percentage

stoichiometry of lead nitrate and sodium sulphide dosing for lead sulphide precipitation.

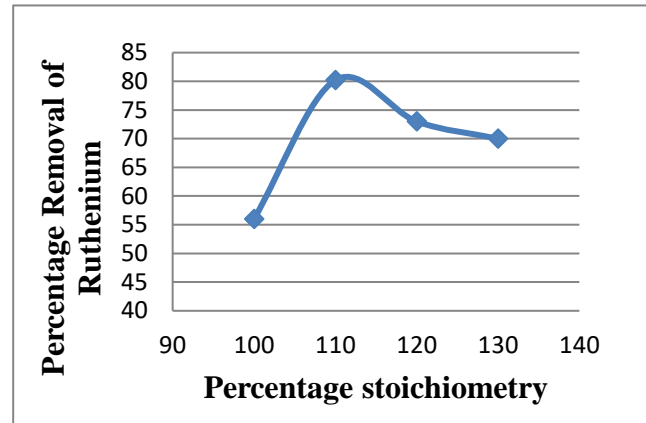


Fig. 4. Percentage Removal of Ruthenium as function of percentage stoichiometry of lead nitrate and sodium sulphide

## 2.4 Kinetics of removal of Ruthenium

In order study the rate of removal of ruthenium by co precipitation process non active trial on the treatment of Ruthenium effluent was carried out. 100 ml of 100 ppm of ruthenium as ruthenium trichloride was treated with 33.1 ppm of lead nitrate and 7.8 ppm of sodium sulphide corresponding to 110% stoichiometry of the precipitation reaction for precipitation of the sulphides at the pH = 4.2. Sampling was done at every 15 minutes. The Percentage removal of Ruthenium as function of time is shown in fig.5.

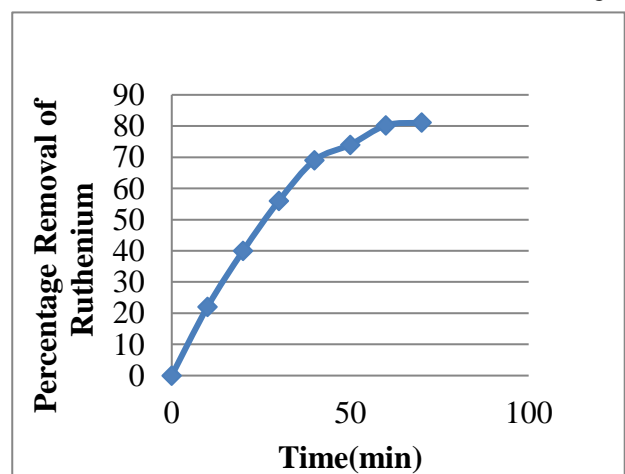


Fig. 5. Kinetics of Percentage Removal of Ruthenium as function of Time

## 2.5 Removal of radioactive $Ru^{106}$ at different initial activities of Ruthenium

Since coprecipitation of lead sulphide is a function of initial strength of Ruthenium, an attempt on the study on the various strength was carried out, experiments were carried out with 25 ml of Ruthenium solutions of strength  $10^{-4}$  -  $10^{-2}$  micro curie/ml at the optimum pH = 4.2. (Table 1) using precipitation of lead sulphide at 110 % stoichiometry. Table 1 shows the Percentage removal of Ruthenium as function of strength of Lead Sulphide.

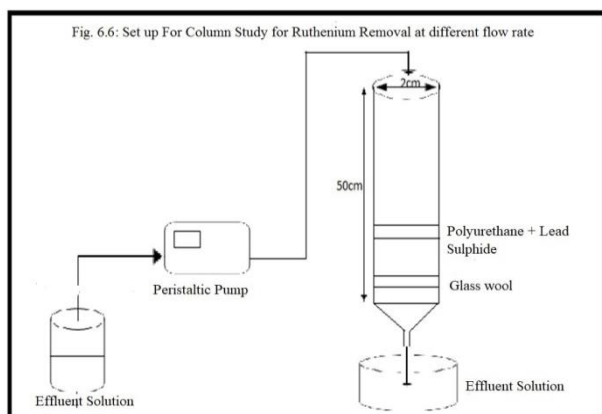


**Table 1. Shows the Percentage removal of Ruthenium as function of strength of Lead Sulphide.**

| Specific activity (μCi/ml) | Percentage strength of Lead Sulphide. | Percentage removal of Ruthenium Activity |
|----------------------------|---------------------------------------|--|
| 10 <sup>-4</sup>           | 36                                    | 54                                       |
| 10 <sup>-3</sup>           | 36                                    | 73                                       |
| 10 <sup>-2</sup>           | 36                                    | 84                                       |

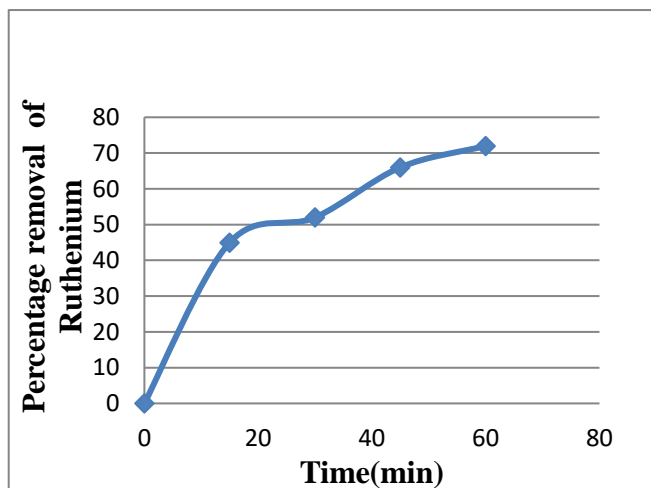
**2.6 Column studies using sulphides coated over PU (poly urethane) foam**

Since the lead sulphides has been proved to be good as a coprecipitant for Ruthenium in the batch study, attempt was made using lead sulphide as column material. Hence in order to make use of lead sulphide as sorbent it was coated over polyurethane foam by equilibrating 100 g of foam of size 2 cm x 2 cm with 0.9 L solution containing 250 ml acetone and 600 ml of ethyl alcohol with 6% poly vinyl alcohol binder and 0.1 Kg of lead sulphide.

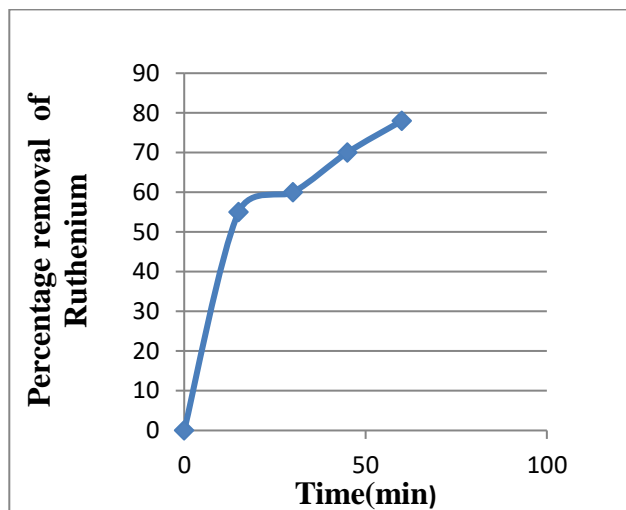


**Fig. 6. Setup for column study for Ruthenium removal at different flow rate**

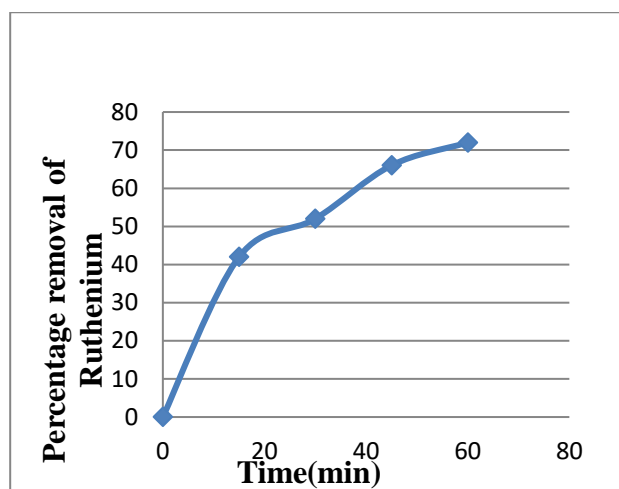
As prepared polyurethane coated with lead sulphide were used in column experiments for the removal of Ruthenium using the column material viz. the lead sulphide coated over polyurethane column was packed in a column giving rise to column of height 10 cm. Ruthenium solutions of strength 10<sup>-2</sup> micro curie/ml was passed at different flow rates 10 BV/h to 30 BV/h using peristaltic pump. Samplings were carried out from the effluent in an interval of 10 minutes and analysed for Ruthenium activity strength. Figs.7a-7c show the removal of Ruthenium as function of time at 10–30 BV/hr.



**Fig.7a: Percentage Removal of Ruthenium of specific activity 10-2 as function of time at 10 BV/h**

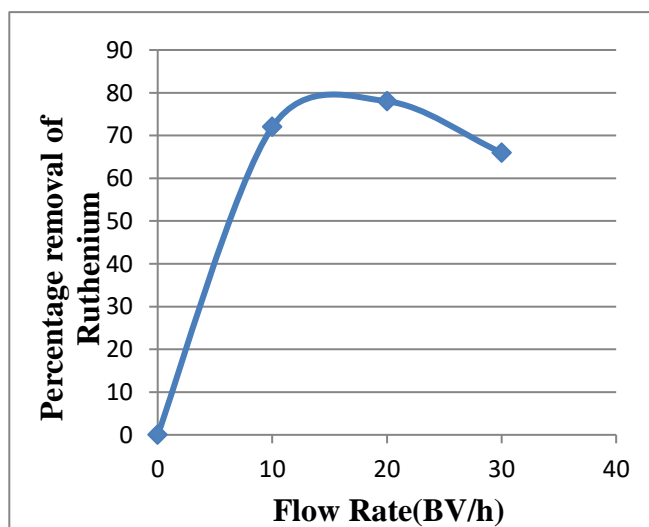


**Fig.7b: Percentage Removal of Ruthenium as function of time at 20BV/h**



**Fig .7c: Percentage Removal of Ruthenium as function of time at 30 BV/h**

Figure.8. shows the Percentage removal of Ruthenium as function of flow rate in 1 hour duration



**Fig. 8. Percentage removal of Ruthenium in 1hr at different Flow Rate**



## III. RESULTS AND DISCUSSION

### 3.1 Settling nature of sulphides

Figure 1 shows the zeta potential of lead sulphide and ruthenium sulphide falling from positive to negative passing through zero value at pH 4.1. Hence for the pH for point of zero charge for both lead sulphide and ruthenium sulphide were found to be at pH around 4.2. Since magnitude of zeta potential at this pH are zero, particles of the lead sulphide can coalesce and settle down at pH 4.2. So the lead sulphide can coprecipitate the Ruthenium along with at this pH. It is found from table 1 the zeta potential of PbS at pH 2 to 6 are -62 mV and 45 mV respectively. Figure 2 shows the particle sizes at these pHs are ranging between 39 nm and 113 nm respectively. For Ruthenium sulphide the zeta potentials at pH=2 to 6 are 10 mV, -25 mV respectively. The particle sizes at these pHs range 123.7 nm 393 nm respectively. Since the magnitude of the zeta potentials at pH=4.2 are less, the particles can coalesce and settle down. So the lead sulphide can coprecipitate the Ruthenium along with it.

### 3.2 Optimisation of pH of the precipitation

For any precipitation, pH plays an important role. Since co precipitation involves inter crystalline precipitation of the precipitates along with precipitates of radioactive ions, pH for co precipitation has to be optimized. The percentage removal of 100 ppm of Ruthenium using 110 % stoichiometry of the precipitants in 60 minutes duration at the function of pH was shown in fig 4. It was found from fig4 that the optimum pH as 4.2. The percentage removal of Ruthenium decreased above pH =4.2. Hence the pH of the removal was optimised as 4.2. This is obvious from the zeta potential measurement also.

### 3.3 Optimisation of dosing of precipitants

It is imperative to optimize the strength of the precipitants on the removal of Ruthenium. For this purpose 100 ppm of ruthenium solution was treated with lead nitrate and sodium sulphide corresponding to 100%, 110%, 120% and 130% stoichiometry for 1 hour. Then the percentage removals were found to be 56, 80.2, 73 and 70. at 100%, 110%, 120% and 130% stoichiometry respectively shown in fig 4. Hence the optimum dosing was fixed at 110 % stoichiometry on the maximum removal of Ruthenium at this pH.

### 3.4 Kinetic Studies

The kinetics studies were carried out at the optimized conditions of pH and optimum strength (i.e.110% stoichiometry). Kinetics of removal of ruthenium was carried out at time interval of 10 minutes (Figure 5). From fig.5 at pH = 4.2 the percentage removal of Ruthenium were in 10 to 70 minutes were found to be 22, 40, 56, 69, 74, 80.2, and 81.1 respectively. With increase in time, the percentage removal of Ruthenium increased since the body available for scavenging the Ruthenium increased with the dosing of the precipitants.

### 3.5 Effect of different concentration of Ru<sup>106</sup>

The study on Percentage removal of Ruthenium as function of Lead Sulphide strength is shown in table 1. From tab1 the percentage removal of Ruthenium at lead sulphide strength of 36 ppm was found to be 84, 73, and 54 using 10<sup>-2</sup>, 10<sup>-3</sup> and 10<sup>-4</sup> micro curie /ml of active Ruthenium solutions at

optimized pH and optimized dosings. The percentage removal of Ruthenium increases with more strength of Ruthenium as the removal of strength is partially co precipitation and partially adsorption as the rate of the reaction is proportional to active mass and hence strength.

### 3.6 Column Studies

The results on the column studies on the removal of Ruthenium using foam coated studies is shown in fig.6 In the column studies mechanism of co precipitation does not hold since the column studies involving removal of Ruthenium by Lead sulphides coated over PU foam by the sorption process. The efficiency of removal is not much and hence it can be used for polishing purpose. At different flow rates 10–30 BV/h, Ruthenium was passed through the column containing foam coated with lead sulphide (fig.7a–7c). The residence time at the follow rate of 10, 20, 30 BV/h are 6 min, 3 min and 2 min. Since larger residence time entails more contact with sulphides coated, the sorption mechanism results in more removal at low flow rates. Since the difference in the residence times with higher flow rates is not much, the more amount of Ru/ml results in more removal. Even though the residence time is less from 10 to 20 BV/h the availability of more Ruthenium with more flow rate increases the percentage removal of Ruthenium from 10 to 20 BV/h beyond which the lesser residence time takes over more Ruthenium ions for removal and so there is reduction in the percentage removal Ru beyond 20 BV/h and so the optimum flow rate was fixed as 20 BV/h. The percentage removal Ruthenium activity was found to be 72, 80 and 69 at flow rates of 10, 20 and 30 BV/hr respectively.

## IV. CONCLUSION

Treatment of ruthenium by coprecipitation using lead sulphide has been found to be satisfactory. Removal of ruthenium will reduce the activity burden making the handling and treatment of radioactive decontaminating effluent easy.

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6. Berak L; Uher E, Marhol M., atomic energy review,1975, 1:325–367radioactive decontaminating effluent easy.

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