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GOVERNMENT OF INDIA
परमाणु ऊर्जा आयोग
ATOMIC ENERGY COMMISSION

STUDIES ON THE TREATMENT OF URANIUM MILL EFFLUENTS

by

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Desalination and Effluent Engineering Division

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1. INTRODUCTION

Radioactive solid and liquid tailings are generated in huge quantities during the milling operations for the recovery of Uranium from its ores[1,2]. After uranium leaching, almost the entire ore fed to the mill is finally rejected as solid waste. Contaminants in the solid tailings are more or less fixed and there is very little possibility of their spread into the environments. Bulk of the solids separated as sand and gravels are used as back fill material for the exhausted mines where they are safely contained. Rest of the solid tailings are either retained in the tailings pond or are utilised for raising the height of the barrage. Apart from solid tailings, every thousand tonne of ore processed generates about three to four thousand cubic meters of liquid effluents which are source of both chemical and radioactive contaminants. Acidic barren liquors produced as ion exchange column effluents constitute major part of the process effluents and contain bulk of the chemical and radioactive pollutants. The present practice followed in their disposal chiefly involves neutralisation with lime and their subsequent transfer into the tailings pond. Such a practice, although helps in retaining major amounts of the contaminants in the pond in the form of sediments, the remaining traces associated with the overflow discharges are still high enough to pose problems of environmental contamination over long periods of time. Another threat to the environmental safety, though small, is from the escape of contaminants through seepages into the ground water.

Among radioactive contaminants, radium is the major offender whereas soluble manganese is chiefly responsible for the chemical toxicity. The tailings pond overflow waters may contain 10 pci/litre or more of radium activity as against maximum permissible discharge limit of 3 pci/litre and about 10 mg/litre of soluble manganese as against the allowable limit of 0.3 mg/litre.

To ensure environmental safety, perhaps, the most realistic approach would be (1) To chemically fix or bind these toxins in a form that may keep them off from redissolving in the pond (2) To prevent accumulation of the contaminants in the pond by removing them prior to their discharge or to decontaminate the overflow waters w.r.t. soluble manganese and radium.

With the above objectives in view laboratory studies were carried out to evolve methods for the decontamination of both barren liquors as well as overflow waters. Further, to prevent leaching of contaminants and their subsequent appearance in overflow waters, attempts have been made to evolve methods for their insolubilisation prior to their release into the pond. Different methods were tried and the results of those studies are discussed in this report.

2. URANIUM RECOVERY PROCESS

The recovery of uranium from its ores is carried out by hydrometallurgical processes. Uranium the valued constituent of the ore is leached by treatment with aqueous solutions. Leach solutions may either be acidic with sulfuric acid or alkaline with mixture of sodium carbonate and bicarbonates. Chemical oxidants are employed to facilitate the leaching process. At Jadugoda[3], Uranium is recovered by the use of acid-leach process as shown in Fig-1. The crushed and ground ore is treated with sulfuric acid in the presence of pyrolusite. Uranium is separated from the leach solutions with the help of ion-exchange processes. Under proper sulfuric acid conditions, uranium is selectively taken up by the exchanger, leaving all radioactive and chemical impurities in solution. Acidic barren solutions produced as column effluents alongwith other process waters constitute liquid tailings. The quantity of liquid tailings approximately equals to the fresh waters used in the plant. Uranium content of the ore processed ranges between 0.05 to 0.7 percent. Thus more than 99 per cent of the ore, on processing, is rejected as solid waste.

3. NATURE OF LIQUID EFFLUENTS

3.1. Mill Effluents

Liquid tailings from the mill may be broadly classified as barren liquors and wash solutions. Ion exchange column effluents constitute the former whereas filter back wash waters, floor washings etc. account for the latter. Barren liquors are essentially leach solutions minus uranium and consequently they contain all the acid soluble chemical and radioactive impurities dissolved from the ore and the oxidant. Type and amounts of the chemical constituents of these effluents mainly depend upon the composition of the ore. Uranium content of the ore determines the extent of radioactive contaminants. Ore analysis as shown in Table-1, indicates that iron, aluminium, calcium and magnesium are the major acid soluble components and therefore are most likely to be present in large amounts in these solutions. In addition, use of pyrolusite as an oxidant may contribute significant amounts of manganese. Radioactivity of these liquids is mainly due to the presence of decay products of natural uranium. Uranium-238, the major constituent of natural uranium, decays by several alpha and beta emissions until it reaches the stable end product lead-206. Among the different decay products, radium has by far the lowest permissible concentrations in water (Table-2). Barren solutions obtained from the mill has been analysed for active as well as inactive constituents. Standard analytical methods[4,5] have been used for this purpose. Calcium and magnesium have been estimated by EDTA titration, manganese has been determined colorimetrically. Radium on concentration has been estimated by a recommended method[6]. Chemical and radiochemical analysis is given in Table-3 & 4. The liquids are highly loaded with dissolved salts and are acidic in nature. The other effluent streams from the mill contain negligible amounts of dissolved salts and activity.

3.2. Tailings Pond Over Flow Waters

Overflow waters from the tailings pond are near neutral and contain large amounts of calcium, magnesium and sulfate (Table-3). These waters are practically free from suspended matter and have good clarity. However Radium and Manganese concentrations are several times higher than the permissible limits.

4. SOLID TAILINGS

After uranium leaching, mill feed, as a whole, along with unused pyrolusite slurry is rejected as solid waste. Solids are further seggregated as sand, gravel and slimes with the help of hydrocyclone. Sand and gravels are sent for back filling the mine and the slimes are discarded into the tailings pond. Sulphate and pyrolusite help in retaining bulk of the radium with the solid tailings.

5. TREATMENT OF BARREN LIQUORS

5.1. Lime Treatment

As the liquids are acidic in nature, the first step towards their disposal essentially involves neutralisation. A good deal of inactive and active impurities precipitate out during this process. As pointed out earlier, radium and manganese are of major interest and hence their behaviour under different conditions of pH and neutralising agents was studied. Lime in powder form and caustic solutions were used for this purpose. It was observed that irrespective of the neutralising agent used, manganese precipitation is complete, only when the pH is 10.5 and above. Under these conditions the treated liquids were found to be free from manganese. In addition gross activity ($DF_{\alpha} = 300$, $DF_{\beta} = 4$) and radium ($DF_{Ra} = 28$) are also removed to an appreciable extent. Results are shown in Table-5. Addition of 12 g/litre of lime (25% calcium oxide content) was found to be necessary for raising the pH to the required value. Thus most of the active and inactive impurities are contained in the precipitates. The volume of the sludges obtained as shown in Table-6 are very large; for example overnight settling of the precipitates resulted in 40-50 percent sludges by volume relative to the solution volumes treated. Some of the sludge characteristics are as under:

Sludge volume (on overnight settling) : 50 percent by volume of the treated liquids

Sludge density : 1.0267 g/cc

Dry extract of the sludge : 66 g/litre

Amount of wet cake (on filtration under vacuum) : 198 g/litre

The above data indicates that filtration of the sludges would give rise to about 100 tonnes of wet cake per day per thousand cubic meters of barren solution. It would amount to about 30 tonnes on dry weight basis.

5.2. Barium Sulfate Treatment

Neutralisation results in large volumes of radioactive sludges requiring special care and heavy expenditure in their handling and disposal. Another alternative would be to concentrate radium in smaller volumes which could be handled with comparative ease. For this purpose radium removal from acid barren solutions was studied by coprecipitation with barium sulfate. Different amounts of barium ranging from 10 to 200 mg/litre were precipitated with stirring and the extent of coprecipitation was determined. Results shown in Table 7a & 7b indicate that a maximum of about [illegible]5 percent radium could be eliminated by the addition of 25 mg/litre of Ba^{2+} ions. Higher amounts did not show any improvement. Sludge volumes on overnight settling amounted to about one percent of the liquid volumes treated. Radium precipitation, however, improved with increase in pH, 98.6% radium removal was obtained on adjusting the solution pH to 5. Sludges produced under these conditions amounted to about 8 percent of the liquids treated. Precipitation is restricted to iron and aluminium whereas the other inactive impurities remain in solution. Further increase in pH increases the sludge volumes without any additional benefit. Thus addition of barium followed by adjustment of solution pH to 5, would eliminate most of radium activity. Active sludges may be separated out and retained for disposal. Such a practice may help in reducing radium load and its further accumulation in the pond.

5.3. Combined Barium Sulfate - Lime Treatment

In order to improve upon the efficiency of lime treatment to insolubilise radium, barium sulfate precipitation was tried in combination with lime. Different amounts of barium were used for this purpose. Introduction of 25 mg Ba^{2+}/litre followed by neutralisation and increase in pH to 10.5 with lime could insolubilise 99.5 percent of radium activity. Results are whown in Table-8. Sludge volumes remained practically the same as obtained during the process of lime treatment alone.

5.4. Treatment With Barytes

Barytes, a naturally occuring mineral of barium, is often suggested for use in the treatment of Waste Waters contaminated with radium activity[7]. Its use in the concentration of radium from acid barren liquors was examined. The important factors studied are contact time, particle size, concentration of barytes and method of contact on the extent of radium uptake. Measured volumes of liquids were contacted with known amounts of barytes(96 percent $BaSO_4$) in powder form and agitated with a mechanical stirring device. Aliquot samples were withdrawn after a fixed duration of time and centrifuged, supernatant was analysed for radium activity. Results shown in Tab[illegible] indicate that a minimum of one hour contact time is necessary to achieve equilibrium. Results in Table 9b and 9c show that the activity removals increase with decrease in particle size and with increase in barytes concentrations. These observations indicate that concentration of radium on barytes is mainly controlled by surface adsorption mechanism. Radium removals upto 88 percent could be achieved on contacting 2 g/litre of barytes of 200 to 325 mesh size for about an hour with barren solutions.

Feasibility of its use in column was also examined. Barytes sample with 40-60 mesh was used for this purpose. Finer fractions could not be used, for acceptable flow rates could not be obtained. 10 gram barytes was packed in a glass column (1.8 cm dia. and 27.7 cm height) and solution was passed through it. Radium uptake under conditions of varying flow rates was studied. Break through ranging between 15 to 20 percent was observed through out upto 500 bed volumes, at the rate of 5 column volumes per hour. There was no significant increase in break through on passing larger volumes of the influents. However, increased flow rates resulted in increased break through values; for example break through of the order of 30 percent was obtained on increasing the flow rate to 10 column volumes per hour.

5.5. Treatment With Pyrolusite

Manganese dioxide has been known for its affinity to fix a number of metal ions on its surface. This property has been suggested for its use as radium collector from the mill effluent[8]. Pyrolusite, a naturally occuring manganese dioxide ore was taken up for studies to concentrate radium from acid barren solutions. Radium uptake was studied both under static as well as dynamic conditions.

Under static conditions, batch of mineral (70% MnO_2) weighing 2 gram was placed in a glass container and stirred with a litre of barren liquor. Equilibrium was achieved within an hour of contact. Different concentrations of pyrolusite and the particle sizes were tried for this purpose. Results are shown in Table-10a & 10b. Radium uptake increases with decreasing size and marginally with increasing concentrations. Removals upto 92 percent were obtained on contacting 2 g/litre of pyrolusite of 400 mesh size. Agitation was stopped after one hour and the slurries were allowed to settle. A clear solid-liquid separation was obtained after about 12 hours of settling. Supernatant was separated and settled slurries were reused for the treatment of a fresh batch. It was observed that its capacity to concentrate radium remains unaffected; for example 87 per cent removal was obtained in the second time treatment. This suggests the reuse of settled slurries in the treatment cycle. Freshly prepared manganese dioxide was also tried for this purpose. It was prepared by the action of hydrogen peroxide on potassium permanganate. The product was washed, dried and powdered. Batch equilibrium tests showed that the laboratory prepared sorbent is superior to the mineral. Under similar conditions of concentrations and time of contact, 96 per cent radium up take was obtained with the freshly prepared sorbent as compared to 92 percent with the mineral.

Under dynamic conditions, sorbent was packed in glass column and sorption was studied with different particle sizes. 40-50 mesh size was found suitable for column use. The finer fractions, due to compression under flow did not work as the acceptable flow rates could not be obtained. However, with the above size, efficiency of radium concentration remained unsatisfactory; for example 40 to 50 percent breakthrough was noticed within first few column volumes.

6. STABILISATION OF MANGANESE

Neutralisation of barren solutions results in the precipitation of manganese(II) hydroxide. It was observed that solubility of the hydroxide decreases with increase in pH as shown in fig. 2. Although, neutralisation to pH 10.5 helps in the complete precipitation of manganese as hydroxide, the fall in pH in the tailings pond brings about its partial resolubilisation. As a result manganese appears in the overflow waters. Manganese (IV) oxide can withstand to the changing solution conditions as it remains insoluble under a wide range of pH. In view of this, it was considered that change of Mn(II) to Mn(IV) would help in stabilising manganese, thus avoiding its redissolution. Methods such as air oxidation, chlorination, permanganate treatment etc. were tried for this purpose.

<u>Air oxidation</u>: Under alkaline conditions, $Mn(OH)_2$, is known for its affinity to react with dissolved oxygen in solutions to form Mn(IV) oxide as per the following reactions.

$$MnSO_4 + Ca(OH)_2 \longrightarrow Mn(OH)_2 + CaSO_4$$

$$2.Mn(OH)_2 + O_2 \longrightarrow 2.MnO(OH)_2$$

Oxidation proceeds stiochiometrically, 1 ppm of dissolved oxygen oxidises 7 ppm of manganous manganese. Considering the large amount of manganese in addition to dissolved oxygen, supply from external sources is necessary to bring about complete conversion to higher oxides.

Air digestion of the neutralised barren slurries was tried. Experimental set up is shown in fig.3. Measured volume (500 ml) of acid barren solution was taken in a glass container of one litre capacity, pH was raised to 10.5 by the addition of lime. Air was passed at a fixed rate for different duration of time. It was observed that, as the aeration proceeds, the precipitates change from dirty brown to greyish black color. This indicates of a change to higher valence state. Extent of stabilisation was determined by acidifying the aerated sample with dilute sulfuric acid to pH 2 - 3. Acidified solutions were stirred for about half an hour and the unaffected precipitates were allowed to settle. Supernatant was analysed for soluble manganese. These amounts were taken as unreacted manganous manganese. Results are shown in fig. 4. Oxidation was found to accelerate after a time lapse of about fifty minutes. This is in accordance with the reported observations, indicating that once the higher oxide is formed, it exerts a catalytic effect and facilitates the process of oxidation. Air digestion of the neutralised slurries at the rate of 85L air/hr for 2 hours, 4 hours and 6 hours resulted in 98, 98.5 and 99.2 percent conversion to higher oxides respectively. It was further observed that air digestion helps in improving settling characteristics as well as reducing the sludge volumes; for example sludges amounting to 35 percent were obtained with aeration as compared to 50 percent without aeration.

Chlorination

Oxidation by direct chlorination was, however, not tried. Commercial grade bleaching powder was used as a source of active chlorine for this purpose. About 1.8 g/litre of bleaching powder (36% available chlorine) was found to be necessary for bringing about complete oxidation of manganese(II) present in the neutralised barren slurries. Conversion in this case was found to be much faster as compared to simple aeration. Settling and filtration characteristics of the sludges also improved significantly.

Permanganate Treatment

Permanganate oxidises Mn(II) both under slightly acidic as well as alkaline conditions. Amounts of potassium permanganate required to completely oxidise Mn(II) in the neutralised barren slurries was found by the dropwise addition of standard permanganate solution till the supernatant acquired persistant pink colour. The liquids were kept stirring during the addition of permanganate. The amounts of potassium permanganate required for the complete oxidation were found to be 131.4 mg/litre. Manganese in acid barren solutions prior to neutralisation could also be oxidised with permanganate. Oxidation under these conditions was found to be faster and more effective than under alkaline conditions.

7. BEHAVIOUR OF MANGANESE AND RADIUM IN THE TAILINGS POND

Neutralised barren solutions along with other liquid tailings are discharged into the tailings pond. Tailings pond at the mill site occupies an area of about 30 acres in a natural depression formed by two hills with an opening on one side[3]. An earthen dam constructed with boulder foundation on the opening side, converts the enclosed area into a pond. In the pond, solid waste settles and the clear liquid overflows into a nearby [illegible]. Although manganese is completely precipitated on neutralisation, it reappears partly in the overflow waters. Partial solubilisation of manganese may be attributed to some in-situ reactions in the pond resulting [illegible] solution conditions. Although [illegible] are highly alkaline($\mathrm{pH} \backsim 10.5$), the overflow waters are normally near neutral($\mathrm{pH} \backsim 7$). This change in pH is possibly responsible for its solubilisation. Neutralising action of atmospheric carbon dioxide on soluble lime seems to be chiefly responsible for the decrease in pH of the pond waters. Calcium carbonate precipitates and settle's during the process. This was verified experimentally. Five litres of barren solutions were taken for this purpose, neutralised and pH raised to 10.5 with lime. [illegible] kept exposed to atmosphere and change in pH was recorded on daily basis. It was observed that the pH decreases to about 7.5 with in a period of 12 days. At this stage the supernatant sample was withdrawn, analysed for dissolved manganese,and were found to contain 8 mg/litre of manganese.

8. TREATMENT OF TAILINGS POND OVERFLOW WATERS

8.1. Manganese Removal

As discussed above, these waters are near neutral and contain upto 10 mg/litre of soluble manganese as against the permissible allowable limit of 0.3 mg/litre. Different alternatives to bring down its concentration before discharge were considered and are discussed below.

Hydroxide precipitation

The concentrations of mangnous manganese in the overflow waters are large enough to permit its precipitation and subsequent removal as hydroxide. Laboratory tests showed that manganese could be completely eliminated by raising the pH of these waters from 7.2 to 10.5. Results are shown in Table-11. It was observed that addition of about 200 mg/litre of lime is required for this purpose. The resulting precipitates had good settling properties and sludges amounted to three percent of the treated waters. Radium activity of these waters however remained unchanged.

Ferric Hydroxide [illegible]

Removal of [illegible] precipitation with ferric hydroxide and ferric phosphate flocs was also studied. 25 mg/litre of ferric iron [illegible] different conditions of pH. [illegible] precipitation was carried out by introducing [illegible] phosphate followed by the addition of [illegible] of ferric iron. It was observed that even in these [illegible] controlling factor. Appreciable manganese [illegible] when the pH is adjusted [illegible]

Permanganate treatment

Another alternative [illegible] manganese by oxidation to higher [illegible] may be carried out with chlorine, [illegible] are effective under [illegible] whereas permanganate can act under wide range of pH and could be employed without changing the actual solution conditions of these waters. [illegible] for example increase in pH would involve [illegible] cost for the chemicals (lime or caustic) needed for this purpose and for the large volumes of sludges requiring further handling and disposal. In view of the above, only permanganate oxidation was tried to optimise [illegible] and the settling [illegible]

To the measured volume of these waters, standard permanganate solution was added with constant stirring, till solutions aquired light pink color persisting for about 10 minutes. Solutions were allowed to stand for the precipitates to settle. It was observed that the precipitates are fine and slow in settling. At least 24 hours settling was necessary for achieving liquid-solid separation. Laboratory tests further indicated that addition of about 6 mg Mn(VII)/litre in the form of sodium or potassium permanganate is sufficient to bring about complete precipitation of the soluble manganese in these waters. The sludge volumes on 24 hours settling amounted to 0.5 percent by volume of the treated liquids. It was also observed that an appreciable amount of radium activity is removed during this process. This observation is in accordance with the reported affinity of hydrous manganese dioxide for radium[11]. Results shown in Table-12, indicate that the treated effluents are free from manganese contamination and the residual radium activity is also much below the permissible discharge limits.

6.2. Radium Removal

8.2.1. Barium Sulfate Treatment

Radium removal from overflow waters was studied by its coprecipitation on barium sulfate. Different amounts of barium ranging from 5 to 75 mg/litre were tried. Results shown in Table-13 indicate that about 90 percent removal is possible by the addition of 10 mg/litre or more of barium. Increase in pH did not show any improvement. Treatment can, therefore, be carried out without changing the existing solution conditions of these waters. Radium activity of the treated waters is below the permissible discharge limits.

8.2.2. Barytes Treatment

Studies on the use of barytes for the concentration of radium from these waters were carried out in a fashion similar to acidic barren solutions. In this case, the studies were restricted to batch equilibrium tests. Among the different sizes tried, a maximum of about 45 percent removal was obtained on contacting 4 g/litre of barytes(-200 mesh) for about [illegible] hours. Removal efficiency reduced to very low values with larger particle size; for example 25 percent removal was obtained with 40-60 mesh.

.2.3. Pyrolusite Treatment

Studies on the use of pyrolusite were also limited to batch equilibrium tests. Among the different fractions tried, best results were obtained with -400 mesh. About 90 percent removal was obtained on contacting 1.5 g/litre of pyrolusite for an hour with constant stirring. An overnight settling is required for the solid-liquid separation. The settled slurries could be reused for the treatment of fresh liquids.

There had been no change in its removal efficiency during 2-3 treatment cycles. Results are shown in Table-14. A slight decrease(~ 10 percent) in soluble manganese was also observed during the process.

9. CONCLUSION

Accumulation of the pollutants may be prevented or minimised by removing them from the effluents before discharge into the tailings pond. Barren liquors may be decontaminated with respect to radium by coprecipitation on barium sulfate or sorption on barytes and pyrolusite. Coprecipitation is effective at pH 5 or above. About 96 percent removal has been obtained by the addition of 25 mg/litre of Ba^{2+} at pH5. Sludges produced under these conditions amounted to about 8 percent of the liquids treated. Precipitation under the conditions of high alkalanity would produce much larger volumes of sludges. Treatment of 1000 M^3 barren solutions would thus produce about 80 M^3 of radium bearing slurries.

Sorption on barytes and pyrolusite is a function of particle size, smaller the size, better is the removal efficiency. Appreciable radium uptake is obtained on their use in sizes less than 125 mesh. Their use in larger particle sizes showed poor performance. These observations rule out the use of these minerals in column or contact beds. These materials in powder form can, however, be used in a batch treatment process. In such a process, they may be contacted with liquids for the desired periods followed by their settling and separation as slurries. The minimum amounts of either of the minerals required for this purpose calculate out to be about 2 tonnes a day.

Similarly manganese may be completely eliminated from the barren solution on its precipitation as hydroxide. Separation and retention of the sludges generated during the above processes would help in controlling the input of the pollutants and their subsequent build up in the pond. Such a practice would,however, give rise to large volumes of sludges amounting approximately to half the liquid volumes treated. Treatment of 1000 M^3 barren solutions, for example; would generate about 400 to 500 M^3 of slurries requiring further handling for their disposal. Such a proposition would complicate the problem rather than providing an economically viable practical solution.

In order to avoid the problem of sludge handling, it is desirable to continue the use of tailings pond as a permanent reservoir for the slurries and the pollutants. Risk of environmental contamination, in this case, may be avoided by chemically fixing or binding the pollutants in a form that keeps them off from redisolving in the pond. Combined barium sulfate-lime treatment could insolubilise radium activity to an appreciable extent in the barren liquids. Radium is homgeneously distributed through out the barium sulfate precipitate and as such there is no possibility of its redissolution in the tailings pond. Combined treatment followed by air digestion of the resulting slurries [illegible] in stabilising manganese(II) to highly insoluble manganese(IV) oxide, thus avoiding the possibility of its solubilisation with change in pH conditions of the pond waters. Residual manganese and radium contamination of the overflow waters could be successfully removed by simple treatment with permanganate solutions and separating the resulting precipitates before their release to the environment.

A treatment scheme as shown in fig.5 have been formulated on these lines. It envisages addition and precipitation of 25 mg Ba^{2+}/litre followed by neutralisation with lime. The sludges on liquid-solid separation are subjected to air digestion for stabilising manganese. Supernatant and the digested sludges are discharged to the tailings pond. Overflow waters from the pond are treated for manganese and radium removal by contacting with 5 to 10 mgs/litre of permanganate. The resulting hydrous manganese dioxide precipitates, amounting to about 0.5 percent by volume of the treated waters which on dewatering may either be used as an oxidant for uranium leaching in the mill or disposed of as radioactive solid waste. The over all cost of chemicals required for the treatment works out to be Rs. 0.30 per cubic meter of the effluents. This would hardly add up any thing appreciable to the cost of production of uranium (Rs. 0.20 to 3.00 per kilogramme of uranium produced)

Decontaminated clean waters may either be released to the environments or reused as process water for milling operations. Its reuse as process water would depend upon the mill specifications for these waters. In case of its being feasible, the contaminants would remain confined to the mill thus ruling out even the slightest possibility of environmental pollution.

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Table - 1

Uranium

Ore analysis

Mineralogical		Chemical	
Constituent	% by Wt	Constituent	% by wt
Quarte	60.0	U3O8	0.07
Chlorite	20.0	SiO2	67.20
Magnatite	9.0	FeO	6.37
Tourmaline	3.5	Fe_2O3	7.87
Apatete	3.0	Al_2O3	5.50
Sulphides	2.0	TiO2	0.66
Cilmenete	1.0	MnO	0.13
Others	1.5	CaO	5.40
		MgO	2.20
		P_2O5	1.04
		S	0.79
		Undetermined	Rest

Table - 2

Maximum Permissible Concentrations

Radionuclide	(MPC) W for unrestricted areas µci/ml
Unat	7×10^{-6}
Th^{234} – Pa^{234}	3×10^{-1}
PO^{210}	3×10^{-6}
Ra^{226}	3×10^{-9}

Table - 3

Chemical nature of the liquid effluents before treatment

Components analysed	Effluent Streams	
	Barren liquors	Tailings pond overflow waters
pH	2.0	7.2
Total dissolved solids g/l	19.6	3.6
Suspended solids mg/l	<5	negligible
Manganese mg/l	560-800	0.4 - 10
Iron mg/l	700-900	Nil
Calcium + Magnesium mg/l	1450	710
Sulphate(SO_4^{2-}) g/l	10-11	1.5 - 2.0

Table - 4

Radio Chemical nature of liquid effluents before treatment

Components analysed	Effluent streams	
	Barren liquors	Tailings pond overflow waters
Gross beta µci/ml	8.16×10^{-5}	1.6×10^{-6}
Gross alpha µci/ml	2.10×10^{-5}	2.3×10^{-7}
Radium-226 µci/ml	1.33×10^{-6}	1.2×10^{-8}

Table - 5

Lime treatment of barren liquors - Removal of active and inactive constituents

Lime added : 12 g/litre

pH : 10.5

Components analysed	Supernatant after lime treatment	Percent removal
Gross beta µci/ml	2.0×10^{-5}	75.00
Gross alpha µci/ml	7.0×10^{-8}	99.70
Radium - 226 µci/ml	4.7×10^{-8}	96.50
Manganese mg/l	nil	Complete

Table - 6

Lime treatment of barren liquors - settling characteristics of the sludges

Solution volume : 100 ml
Lime added : 1.2 gram
pH : 10.5

Settling period in minutes	Sludge volume in ml	
	Sample 1	Sample 2
10	94.0	94.2
20	85.0	86.0
30	81.0	82.0
60	73.5	74.0
90	68.0	69.0
120	62.5	60.0
Over night	48.5	50.0

Table 7a

Barium sulfate treatment of barren liquors - Radium removal

pH = 2 (original)

Amounts of Ba^{2+} added mg/l	Treated solutions	
	Radium-226 activity μci/ml	Radium removal percent
10	4.02×10^{-6}	69
25	3.29×10^{-7}	75
50	3.40×10^{-7}	74
75	3.60×10^{-7}	79
100	3.30×10^{-7}	75
200	3.10×10^{-7}	76

Table 7b

Barium sulfate treatment of barren liquors - Effect of pH

Amount of Ba^{2+} added: 25 mg/l

pH	Sludge volume (over night settling) relative to liquids treated. Percent	Treated liquids	
		Radium activity µci/ml	Radium removal percent
2.0	0.7	3.29×10^{-7}	75.0
3.0	1.2	3.12×10^{-7}	76.0
3.5	1.5	1.90×10^{-7}	85.4
4.0	4.3	1.3×10^{-7}	90.0
4.5	6.8	5.2×10^{-8}	96.0
5.0	8.0	1.80×10^{-8}	98.6
7.0	32.0	1.50×10^{-8}	98.8
9.0	41.0	1.30×10^{-8}	99.0

Table - 8

Combined barrium sulfate and lime treatment of Barren liquors.

Amounts of Ba^{2+} added mg/l	Amount of lime added g/1	pH	Treated liquids	
			Radium activity /uci/ml	Radium removal percent
nil	12	10.6	4.8×10^{-8}	96.30
10	12	10.6	2.3×10^{-8}	98.20
25	12	10.6	6.5×10^{-9}	99.50
50	12	10.6	5.6×10^{-9}	99.57
75	12	10.6	6.8×10^{-9}	99.48
100	12	10.6	5.2×10^{-9}	99.6

Table - 9a

Treatment of acid barren solutions with barytes - Effect of contact time on radium removal

Contact time in min.	Activity removal percent		
	Radium-226	Gross Alpha	Gross Beta
5	51.5	37.0	39.0
10	64.0	39.5	45.5
30	76.0	41.0	50.2
60	80.0	43.0	48.0
240	80.0	41.5	51.5

Table - 9b

Treatment of acid barren solution with barytes

- Effect of particle size

Amounts of barytes used: 2 g/l

Contact time : 60 min

Particle/mesh size	Treated liquids	
	Radium-226 activity /uci/ml	Radium removal percent
- 40 + 60	2.86×10^{-7}	78.0
- 60 + 100	2.54×10^{-7}	80.5
-100 + 150	2.34×10^{-7}	82.0
-150 + 200	1.82×10^{-7}	86.0
-200 + 325	1.59×10^{-7}	88.0

Table 9c

Treatment of acid barren solutions with barytes

- Effect of the amounts of barytes

Time of contact : 60 min

Particle size: 100-150 mesh

Amounts of barytes g/l	Treated liquids	
	Radium-226 activity µci/ml	Radium removal percent
1.0	3.38×10^{-7}	74.0
2.0	2.47×10^{-7}	81.0
3.0	1.81×10^{-7}	86.0
4.0	1.43×10^{-7}	89.0
10.0	1.58×10^{-7}	68.0

Table - 10a

Treatment of acid barren solution with pyrolusite

- Effect of particle size on radium removal

Amounts of pyrolusite used: 2 g/l
Time of contact : 60 min.

Particle/mesh size	Treated liquids	
	Radium-226 activity μci/ml	Radium removal percent
-60 + 100	4.68×10^{-7}	64.0
-150 + 200	2.93×10^{-7}	77.5
-200 + 325	2.28×10^{-7}	84.0
-400	0.975×10^{-7}	92.5

Table 10b

Treatment of acid barren solution with pyrolusite

-Effect of amount of pyrolusite on radium removal

Time of contact : 60 min

Size : -400 mesh

Amounts of pyrolusite g/1	Treated liquids			
	First time treatment		Second time treatment *	
	Radium-226 activity μci/ml	Radium removal percent	Radium activity μci/ml	Radium removal percent
0.5	1.3×10^{-7}	90.0	2.34×10^{-7}	82.0
1.0	0.91×10^{-7}	93.0	2.08×10^{-7}	84.0
2.0	1.04×10^{-7}	92.0	1.69×10^{-7}	67.0
4.0	0.91×10^{-7}	93.0	2.82×10^{-7}	86.0

*Settled slurries from the first treatment are reused for the treatment of fresh liquids.

Table - 11

Tailings pond overflow waters precipitation of Mn(II) as hydroxide

Initial concentrations of Mn(II): 10 mg/l
pH adjusted with lime

pH	Treated waters	
	Conc. of Mn(II) in solution mg/l	Mn(II) precipitated percent
7.2	10.0	-
7.5	8.7	13.0
8.0	8.3	17.0
8.5	7.9	21.0
9.0	6.2	38.0
9.5	4.3	57.0
10.0	0.2	98.0
10.5	nil	100.0

Table ,2

Tailing pond effluents-Removal of manganese and Radium by permanganate treatment

Mn^{2+} : 10 mg/1 } Before treatment
pH : 6.8

Amounts of Mn(VII)added mg/I	Mn(II)in the treated waters mg/I	Radium-226 in the treated effluents /uci/ml
4	0.08	3.5×10^{-10}
5	ND*	3.0×10^{-10}
6	ND	2.9×10^{-10}

*ND-Not detected

Table - 13

Barium sulfate treatment of tailings pond overflow waters

-Removal of radium activity

PH : 7.2

Amounts of Ba^{+2} added mg/I	Treated waters	
	Radium-226 activity $\mu ci/ml$	Percent radium removal
5	2.64×10^{-9}	78.0
10	1.31×10^{-9}	89.0
25	0.96×10^{-9}	92.0
50	1.02×10^{-9}	91.5
75	1.20×10^{-9}	90.5

Table - 14

Teilings pond over flow waters-Radium removal by treatment with Pyrolusite

Time of contact : 60 minutes
pH : 7.2
Size : -400 mesh

Amounts of Pyrolusite g/l	Treated waters			
	First time treatment		Second time treatment *	
	Radium-226 μci/ml	Radium removal percent	Radium-226 μci/ml	Radium removal percent
0.1	3.84×10^{-9}	68.00	4.2×10^{-9}	65.00
0.2	2.88×10^{-9}	76.00	2.64×10^{-9}	78.00
0.5	1.8×10^{-9}	85.00	2.04×10^{-9}	83.00
1.0	1.32×10^{-9}	89.00	1.68×10^{-9}	86.00
1.5	0.96×10^{-9}	92.00	1.2×10^{-9}	90.00
2.0	0.96×10^{-9}	92.00	1.08×10^{-9}	91.00

*Settled slurries from the 1st time treatment are contacted with fresh waters in the second time treatment.

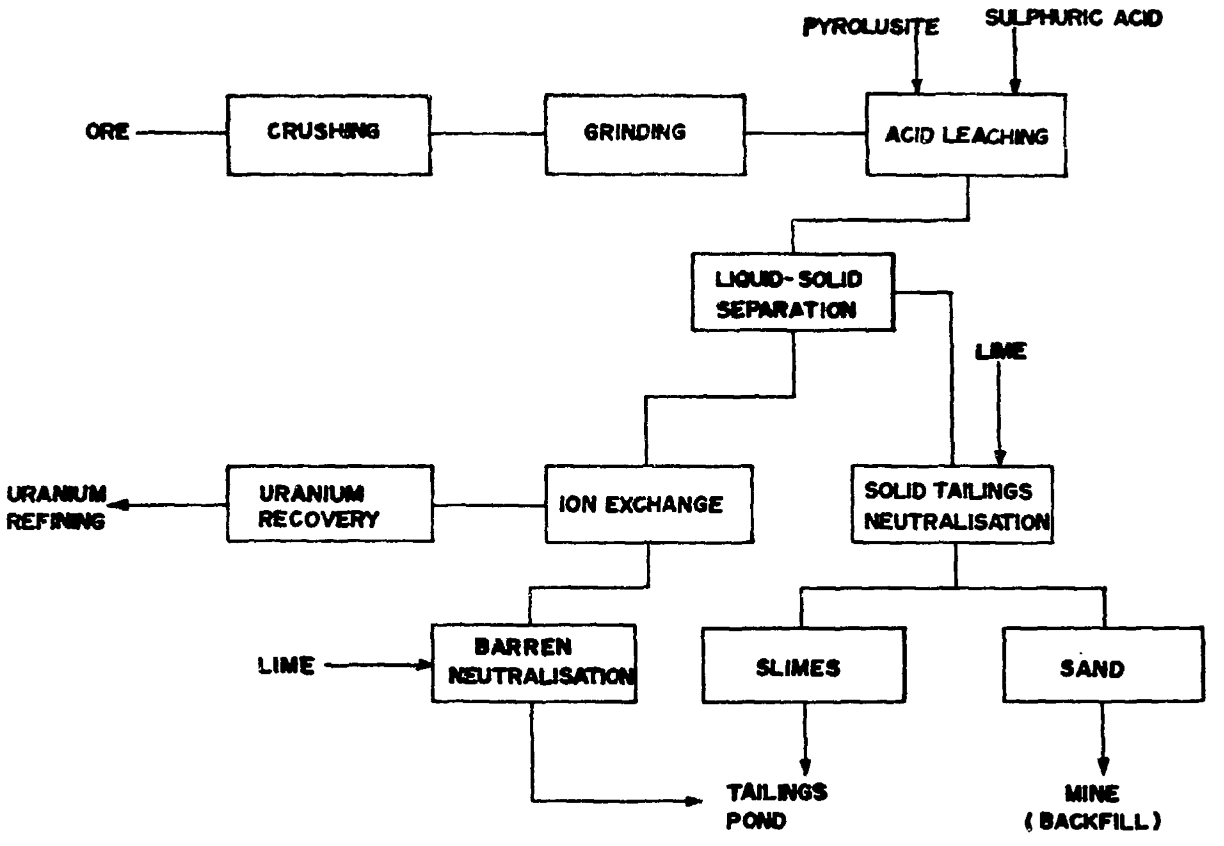


FIG. 1 URANIUM RECOVERY PROCESS

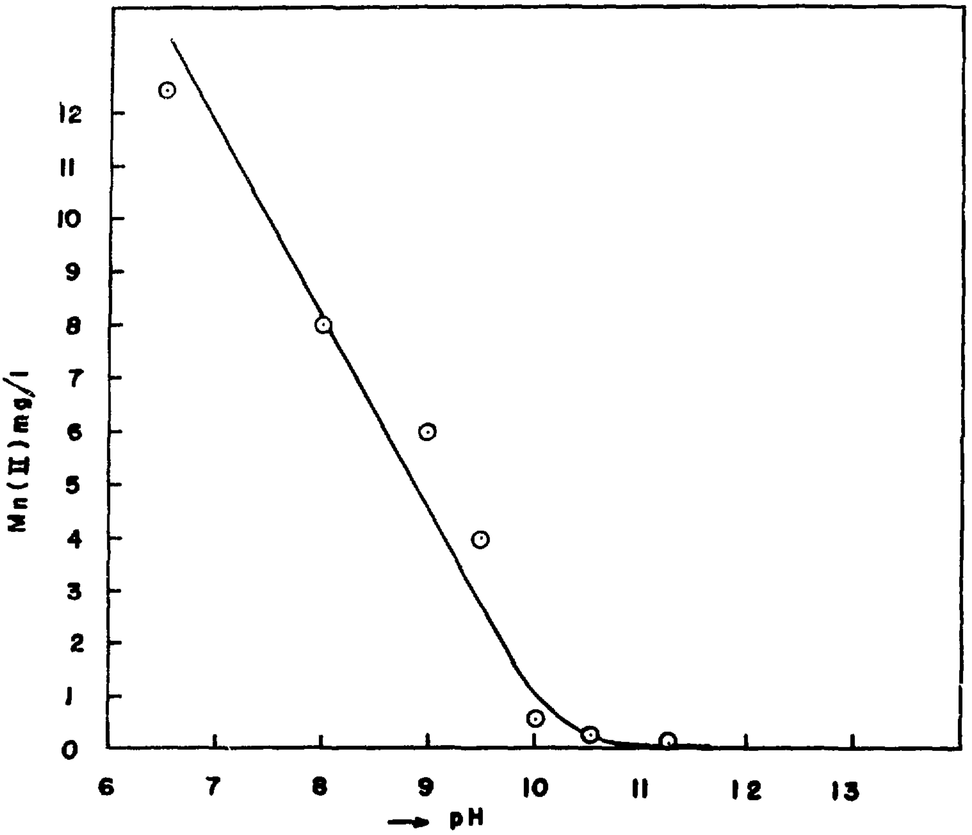
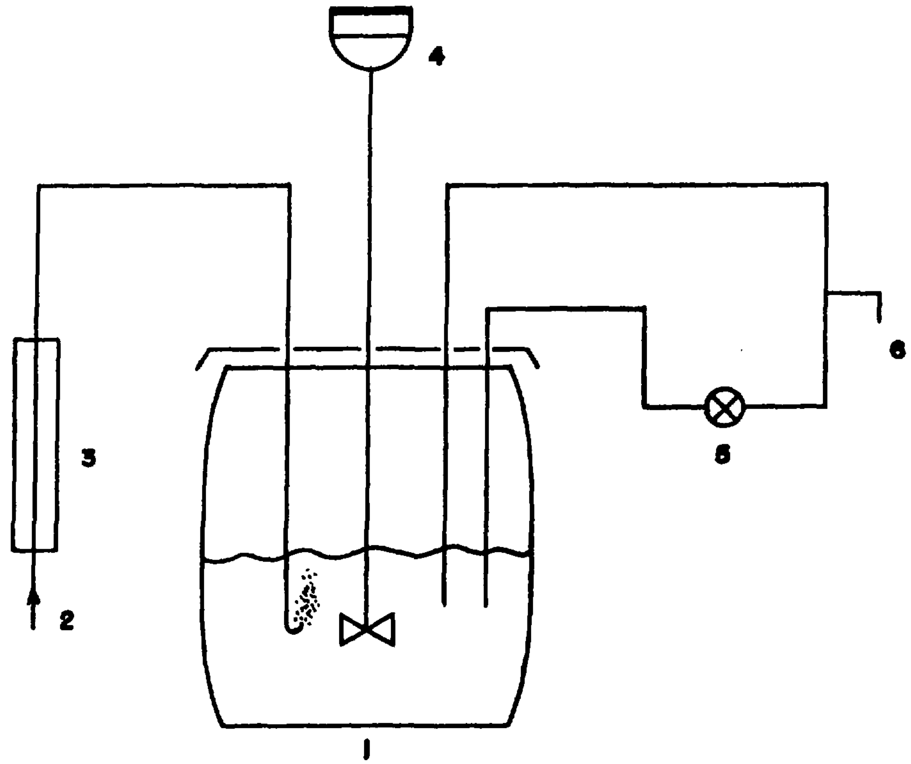


FIG.2 SOLUBILITY OF $Mn(OH)_2$



LEGEND

1. GLASS CONTAINER – I LITER CAPACITY
2. AIR
3. GAS FLOW METER
4. STIRRER
5. RECIRCULATION PUMP
6. SAMPLE COLLECTION

FIG.3 EXPERIMENTAL SET UP FOR AIR DIGESTION

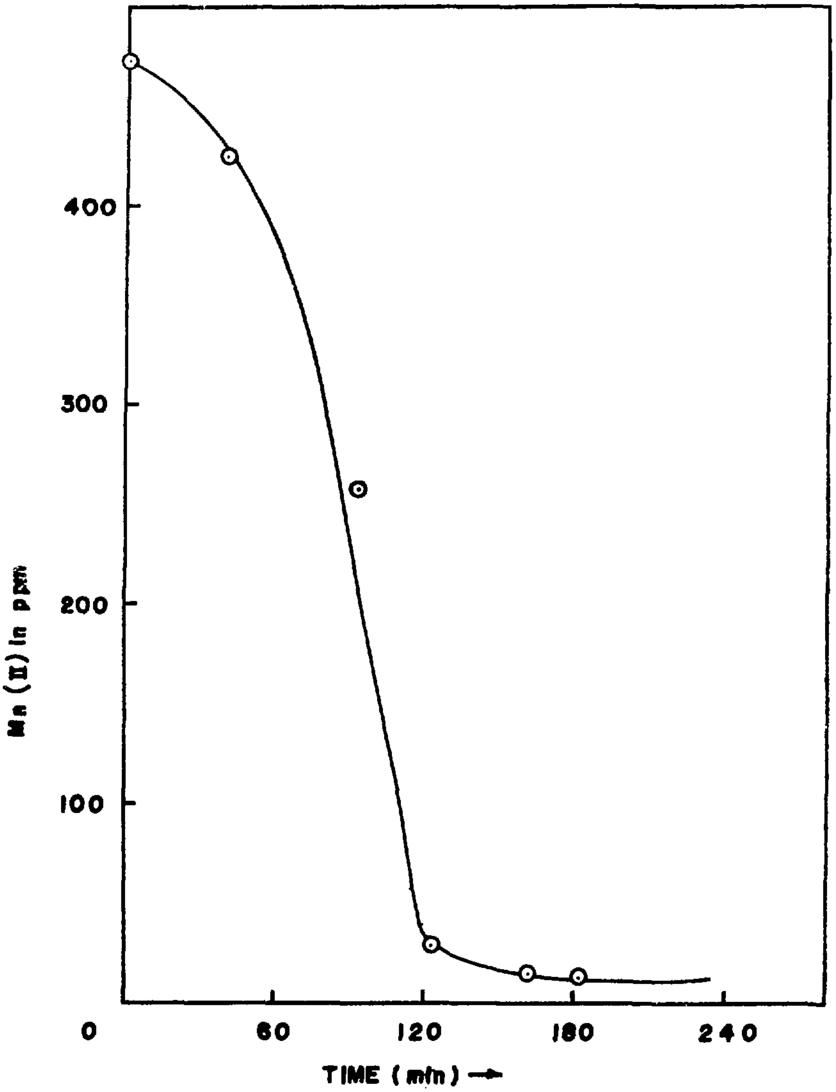


FIG. 4. STABILISATION OF Mn(II) IN NEUTRALISED BARREN SOLUTION

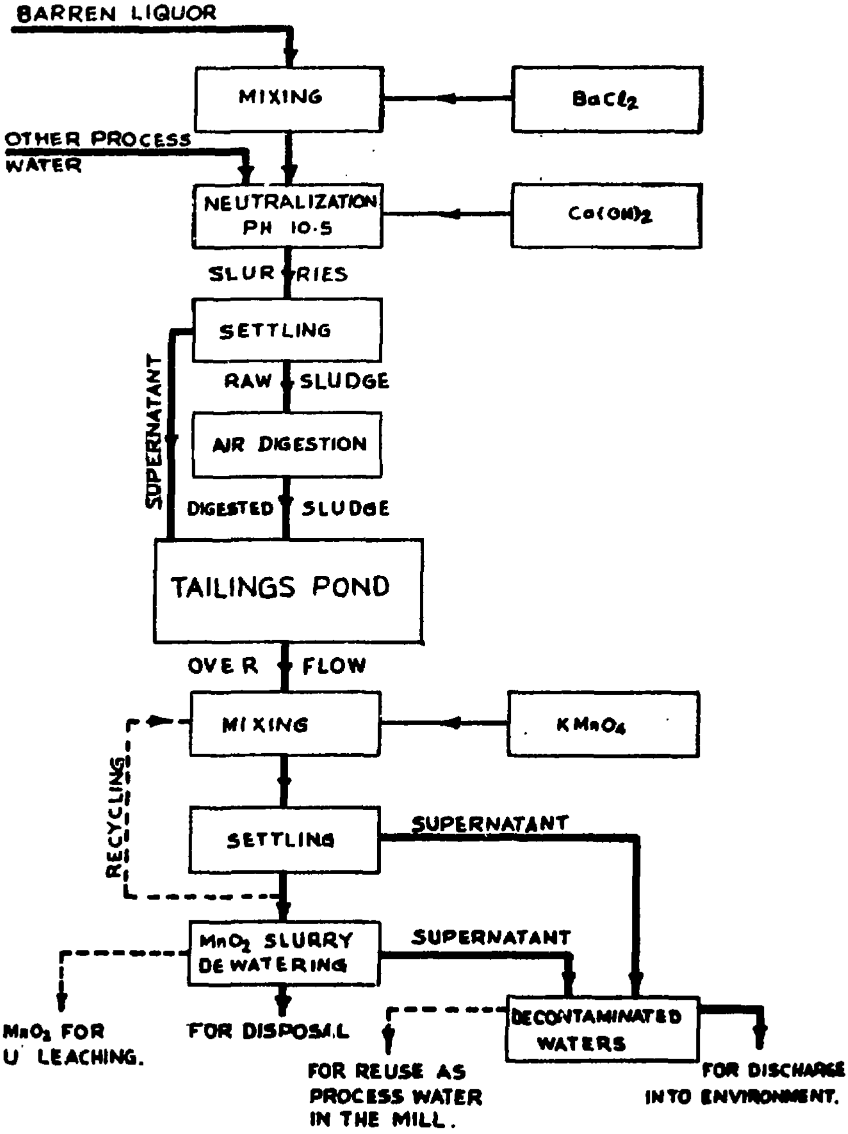


FIG.5
TREATMENT OF URANIUM MILL EFFLUENTS - PROPOSED SCHEME.