APPLICATION OF RESIN IN PULP TECHNIQUE FOR ION EXCHANGE SEPARATION OF URANIUM FROM ALKALINE LEACHATE

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OVERVIEW OF PRESENTATION

- Background to Uranium Ore Processing
- Resin-in-Pulp Process.
- Batch Testing
  - Screening of Resins
  - Parameters influencing Loading of Uranium
  - Elution of Loaded Uranium
- Semi-continuous runs (Carousel Model)
- Conclusions

MOTIVATION ...

Per-capita energy consumption of a country is an indicator of societal development.

The growing energy demand in highly populated developing countries like India calls for a holistic approach in the choice of energy sources. Development should not damage the delicate eco balance.

Seen in this perspective NUCLEAR ENERGY which is reportedly of less carbon foot-print has to be fully and responsibly utilized for energy needs.

The basic fuel element for Nuclear Power is URANIUM.

The motivation for the present work is development of process schemes for the extraction of uranium from various natural resources by energy efficient and cost effective technologies.

URANIUM ORE PROCESSING …

The extraction of uranium from natural resources is accomplished by hydrometallurgical processing

The basic steps include liberation – dissolution – separation of uranium laden solution – purification – precipitation.

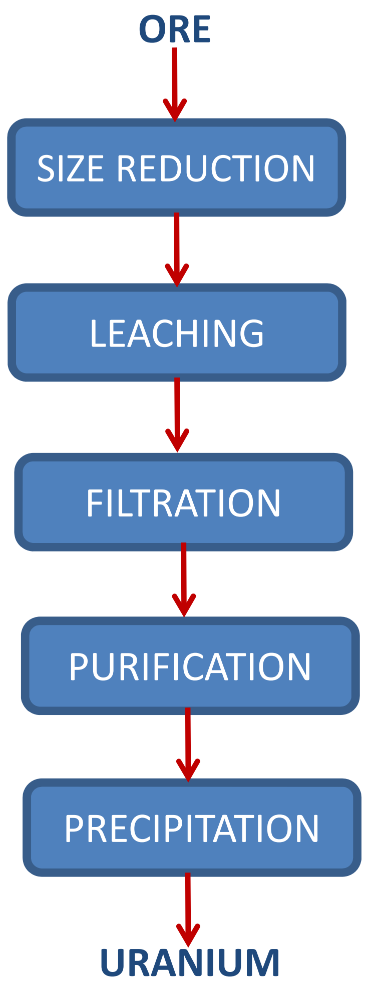
Amongst these operations, the comminution and filtration are very cost intensive.

Any technology which improves the efficiency of comminution and/or filtration is always welcome.

The need for "technological improvements" and "new process alternatives" are all the more important while processing lean tenor ores as well as ores with fine dissemination of valuable minerals in the host matrix.

One such technology entering or re-entering the hydrometallurgy industry is the "Resin-in-Pulp" process.

Hydrometallurgy Scheme for Uranium Extraction



RESIN – IN – PULP PROCESS

The "Resin-in-Pulp" process can yield purified and enriched metal solutions like conventional static-bed ion exchange process eliminating the steps of primary filtration and clarification. Further, it is more attractive option for ores of very-fine grinds which are difficult to thickening or filtration.

The general chemical reaction of ion exchange:

Cation exchange

$nRA + B^{n+} = R_nB^{n+} + nA^+$

or

Anion exchange

$nRA + B^{n-} = R_nB^{n-} + nA^-$

Where:

R - ionized resin molecule with an attached functional group;

A^+ / A^- - exchangeable ion;

B^{n+} / B^{n-} - cation/anion dissolved in the liquid;

n+ /n- - electrical charge of the ion B.

RESIN – IN – PULP PROCESS

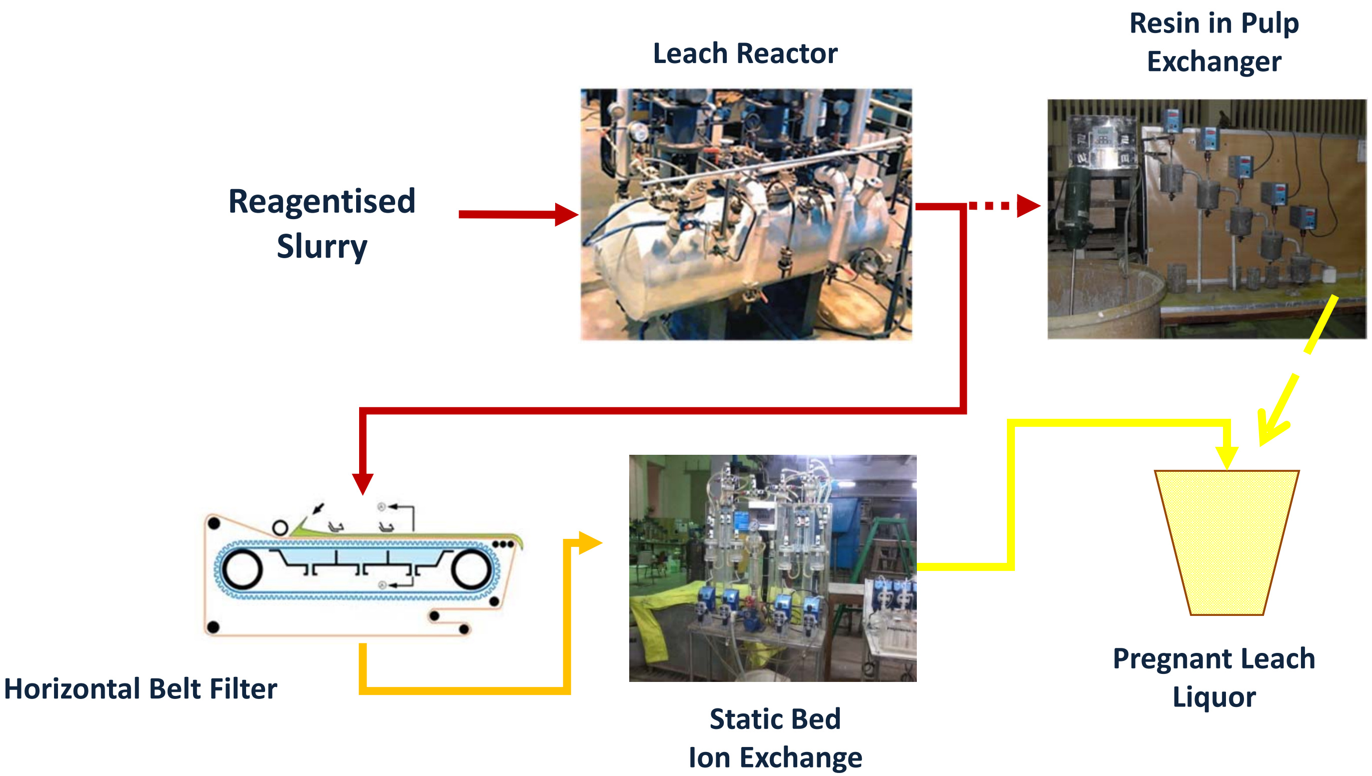
The resurgence of Resin-in-Pulp technology in gold and uranium industry is mainly due to two advancements – (i). Development of mechanically resilient polymer beads and (ii) Resin transfer pumps.

Already many upcoming uranium ore processing plants in Canada, Australia and South Africa are adopting the "RIP" process.

Some examples of such plants are:

URANIUM MILLS WITH "RESIN IN PULP TECHNOLOGY"	
PLANT	COUNTRY
Michelin Uranium Project	Canada
Harmony One Plant	South Africa
Mantra Resources	Australia
Kayelekera Uranium Plant	Malawai, South Africa

STATIC BED AND RIP ION EXCHANGE SYSTEMS



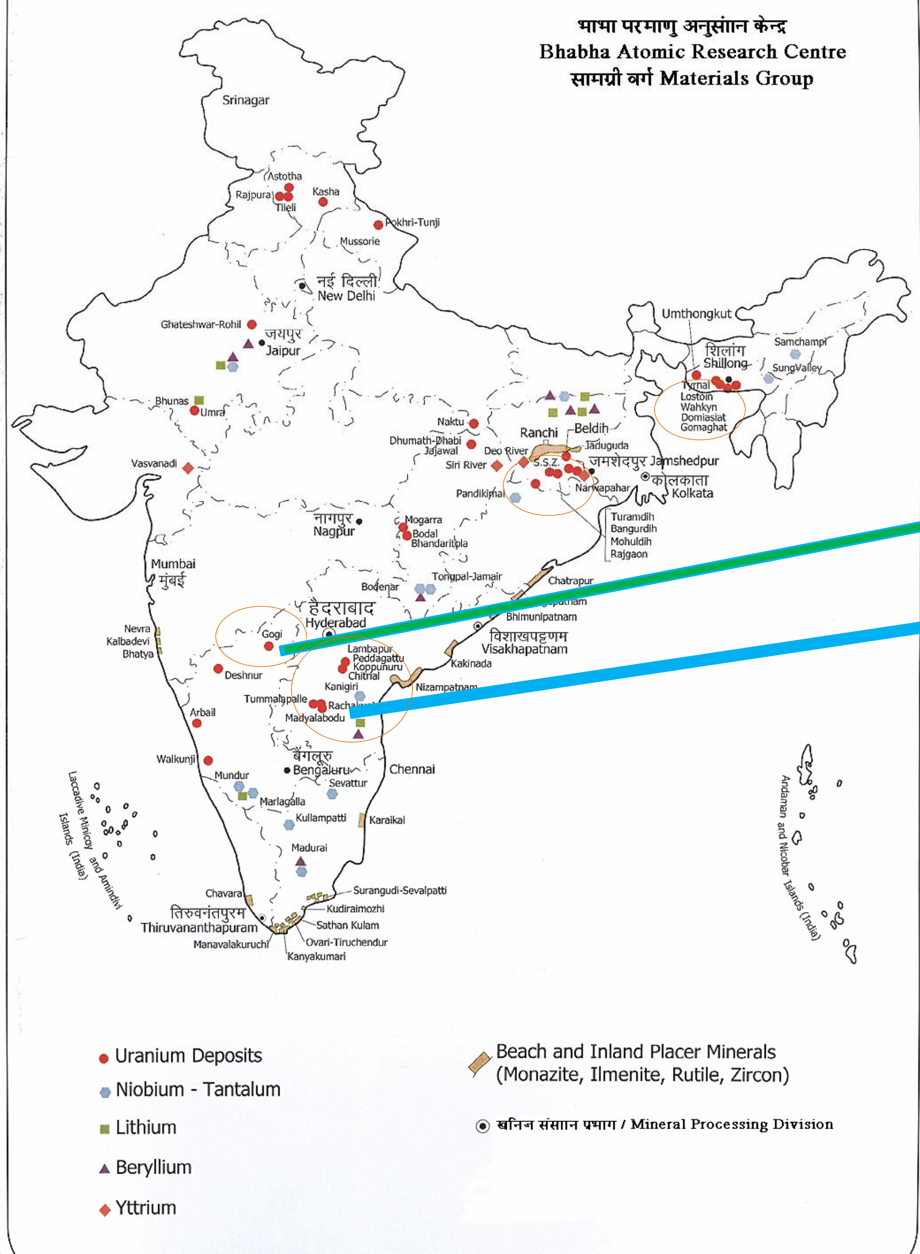
NUCLEAR POWER IN INDIA AND URANIUM FUEL REQUIREMENTS

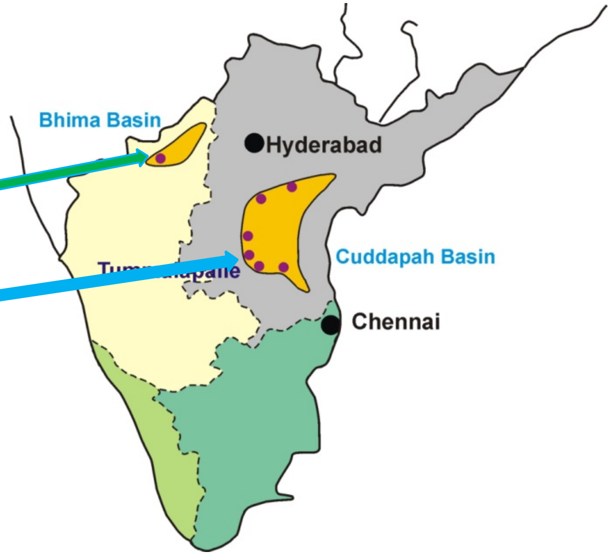
India has an ambitious program aimed at contributing about 30% of the overall power requirements through nuclear energy by 2032.

Practically all the uranium resources, about 1 72 000 tonnes of U_3O_8 discovered so far are low-grade and low- to medium-tonnage variety only.

As part of the expansion program emphasis is being given to new uranium ore deposits located at Tummalapalle (Andhra Pradesh) and Gogi (Karnataka) in southern part of the country.

URANIUM OCCURRENCES IN INDIA





Tummalapalle and Gogi Uranium Deposits in Southern India together contribute about 40% of country's uranium resources.

URANIUM ORE DEPOSITS OF INDIA – NEED FOR RIP

The nature of uranium mineralization in Tummalapalle and Gogi deposits necessitated application of alkaline process, as the host rock is predominantly of carbonate minerals.

Fine grinding of the ore was found essential for adequate exposure of the uranium phases.

The fine size range of the particulate matter and high viscosity of the alkaline solution made filtration of the leach slurry an arduous task.

Filtration on HBF showed need for specialized chemical flocculants and filtration under hot conditions (55 - 60^0 C) for the separation of pregnant leach solution from the leach slurry. Even after adopting these conditions the rate of filtration was only 350 - 500 kg/h-m^2.

Hence, there is a strong incentive to look into alternatives to the cost-intensive filtration process.

URANIUM ORE DEPOSITS OF INDIA – NEED FOR RIP

FILTRATION OF LEACH SLURRY BEHAVIOR ON HORIZONTAL BELT FILTER

BATCH TEST WORK

The leach slurry used in the RIP studies was obtained by subjecting a medium grade uranium ore to atmospheric alkaline leaching using sodium carbonate and sodium bicarbonate leachants in the presence of air.

The mineralogical composition of the ore, granulometry of leach solids or residue and the partial chemical composition of the leach slurry is given in following slides.

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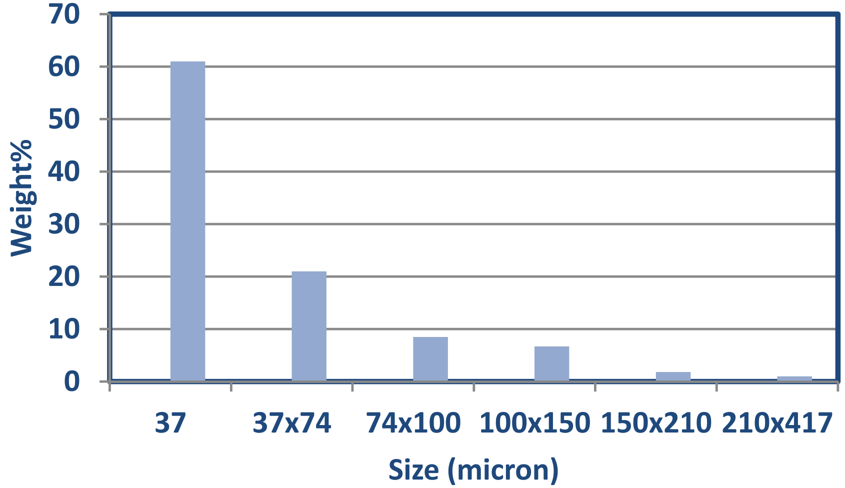
MINERALOGICAL COMPOSITION

Mineral	weight %
Calcite	61.57
Quartz+chert	13.10
Feldspars	1.59
Micaceous minerals (chlorite, biotite and clay)	5.89
Ferromagnesian minerals (mainly hornblende with minor epidote)	0.37
Barite	0.64
Zircon	0.08
Oxides (Magnetite, hematite and goethite)	0.45
Sulphides (Pyrite, marcasite, chalcopyrite and traces of galena)	6.13
Radioactive minerals (Coffinite, pitchblende and adsorbed uranium in association with carbonaceous matter and goethite.)	0.88
Others (determined by difference)	9.3

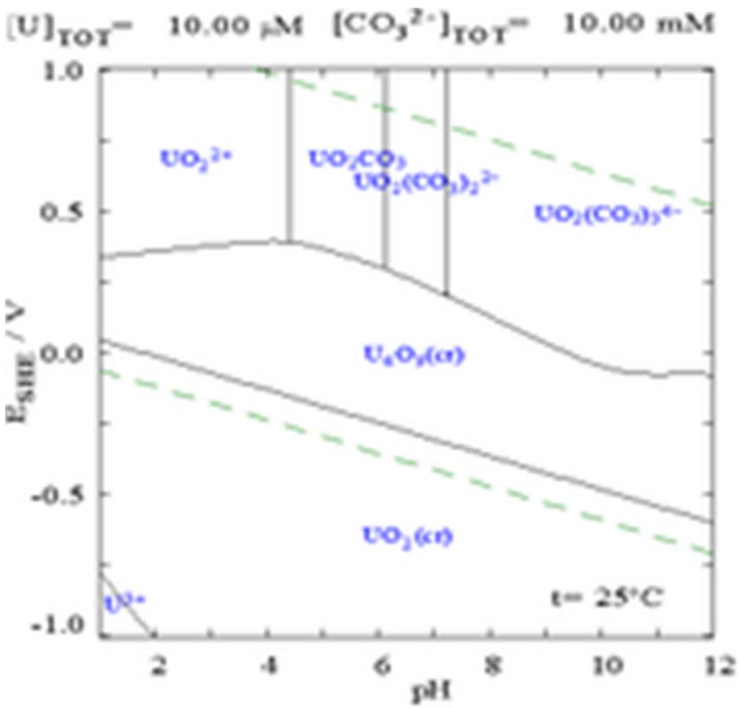
PARTICULATE AND CHEMICAL CHARACTERSTICS

The d_{50} and d_{80} particle sizes of the solids in the leach slurry is 34 & 75µm respectively.

The Eh and pH of the leach slurry indicates that the predominant uranium species present in the solution is Uranyl carbonate – $UO_2(CO_3)_3^{-4}$



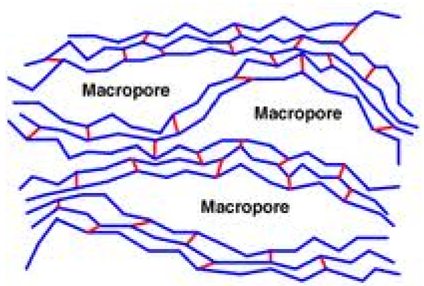
Analyte	Conc. (g/L)
U_3O_8	0.734
Na_2CO_3	36.5
$NaHCO_3$	14.5
Na_2SO_4	2.0
Total Dissolved Solute	46.5
pH	9.5
Eh	110 mV



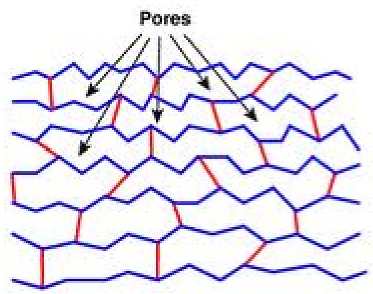
EXPERIMENTAL DETAILS		
Resin-in-Solution	✓ Screening of Resins ✓ Loading Capacity ✓ Kinetics of Loading ✓ Resin to liquor ratio ✓ Number of Stages	Shake flask
Resin-in-pulp	✓ Loading under optimum conditions	Stirred Reactor
Static-bed Elution		Column

SCREENING OF RESINS

- ✓ Based on extensive published scientific literature and product brochures of reputed resin manufacturers, a set of strong base anion exchange resins, both macro-porous and gel type, were chosen for their suitability for uranium ion adsorption in the specific leach slurry under study.
- ✓ A typical affinity series for commonly occurring ions in alkaline leach pulps towards any strong base anion exchange resins is: $V_2O_7^{4-} > [UO_2(CO_3)_3]^{4-} > MoO_4^{2-} > [UO_2(CO_3)_2]^{2-} > SO_4^{2-} > CO_3^{2-} > NO_3^{-} > Cl^{-} > HCO_3^{-}$
- ✓ The macroporous resins investigated include: $920USO_4$, $920UHCSO_4$, 920UCl, IRA910UCl and A500/2788.
- ✓ The gel type resins tested are: ARU103, PFA4740, PFA4783, $400SO_4$ and $4400HCO_3$.



Mechanically strong due to high cross-linking but less exchange capacity



Mechanically less strong due to less cross-linking. Exchange capacity is higher than macroporous.

CHARACTERISTICS OF RESINS - GEL

Name of the Resin	PFA460 / 4783	PFA600 / 4740	ARU 103	(TM) 400 SO_4	(TM) 4400 HCO_3
Manufacturer	Purolite	Purolite	Ion Exchange, India	Rohm and Haas	Rohm and Haas
d_{50} µm	550	600	550	650	550
ρ,g/l (based on dry resin > 600µm)	675	675	680	730	730
Theoretical capacity eq/L	1.60	1.30	1.30	1.4	1.4
Moisture retention capacity %	40-45	47-54	47-52	40-47	40-48
Max reversible swelling Cl^- to OH^- %	20	20			10-15
Matrix	Gel polystyrene crosslink with DVB	Gel polystyrene crosslink with DVB	Gel Styrene EDMA copolymer, isoporous	Gel Polystyrene DVB copolymer	Gel Styrene DVB copolymer
Functional group	Quaternary Ammonium ion	Quaternary Ammonium ion	Quaternary Ammonium ion	Quaternary Ammonium ion	Trimethyl ammonium ion

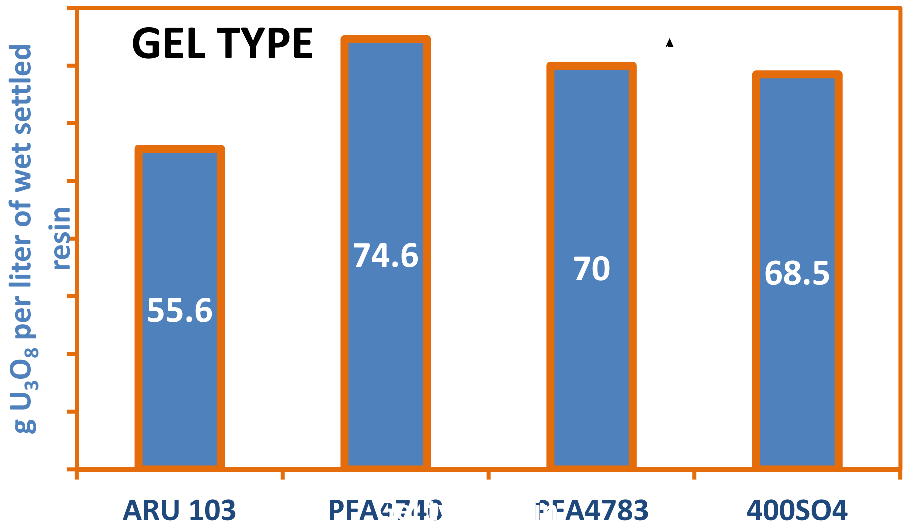
CHARACTERISTICS OF RESINS - Macroporous

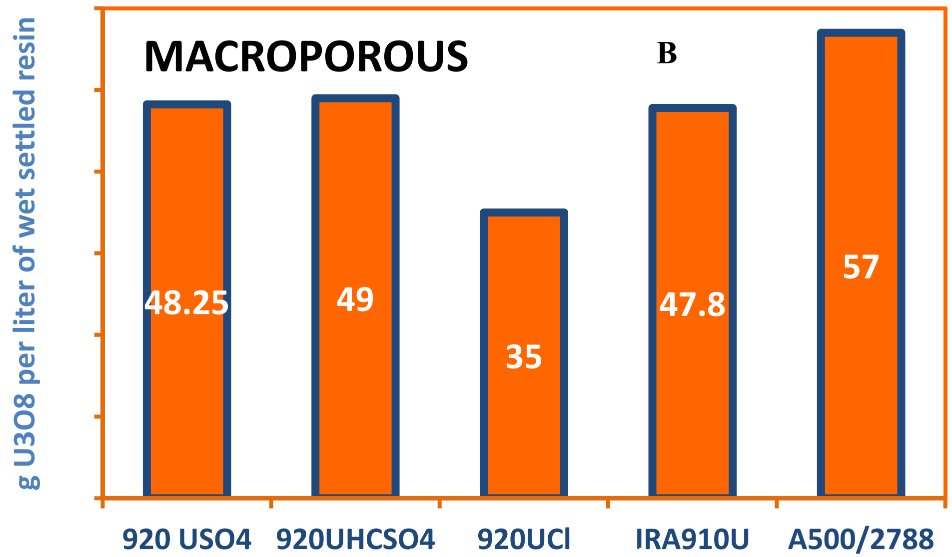
Name of the the resin	Purolite A500/2788	$^{(TM)}$920U Cl	$^{(TM)}$920U $HCSO_4$	$^{(TM)}$920U SO_4
Manufacturer	Purolite	Rohm and Hass	Rohm and Hass	Rohm and Hass
$d_{50}\mu m$	900	850	850	850
r,g/l (based on dry resin > 800μm	675	700	693	735
Theoretical capacity eq/L	1.15	1.0	1.0	1.0
Moisture retention capacity %	53-58	48-60	48-60	48-60
Max reversible swelling Cl^- to OH^-% or Cl^- to SO_4^{2-}	15	20	-	5
Matrix	Macroporous polystyrene crosslink with divinylbenzene	Macroreticular crosslinked polystyrene	Macroreticular crosslinked polystyrene	Macroreticular crosslinked polystyrene
Functional group	Quarternary Ammonium Ions			

SCREENING OF RESINS

The screening of various resins was carried out by equilibrating 1 ml of the respective resin with 100 ml of leach solution for 2 h per stage at ambient temperature. The loading was carried out for six stages amounting to total contact time of 12 h.

The performance was evaluated on the basis of U_3O_8 loading on the resin only.





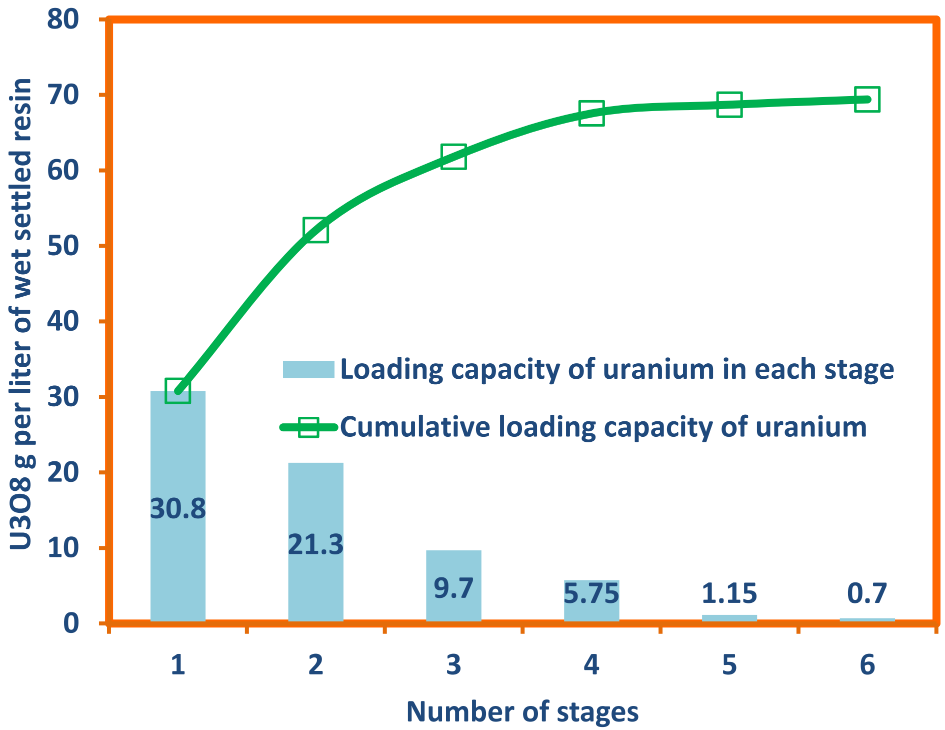
SCREENING OF RESINS

- The gel-type resins showed more uranium loading over the macroporous resins.
- The loading capacity of U_3O_8 was about 70 g/L of wet settled resin (w.s.r.) for the gel type excepting the ARU 103 resin. The ARU 103 gave a loading capacity of only 55 gU3O8 /L of w.s.r.
- The macro-porous resins gave inferior loading, in the range of 40 – 50 gU3O8 /L of w.s.r.
- The sub-optimal loading capacity of macroporous resins is mainly attributed to the lower number of functional groups present in them in comparison to the gel type resins for a given unit weight.
- Since both PFA600/4740 and PFA 460/4783 resins have similar physical properties and uranium loading capacity, one of them, viz. PFA460/4783 was taken for detailed parametric variation study.

LOADING CAPACITY PROFILE FOR PFA 460/4783

The loading of uranyl carbonate anion – $[UO_2(CO_3)_3]^{4-}$ on PFA460/4783 resin was estimated by equilibration of 1 ml of the resin with 50 ml of leach solution at ambient temperature for 120 minutes per stage. The maximum loading capacity of PFA460/4783 was observed to be about 70 g U_3O_8 /L of w.s.r. The saturation was achieved in 4 stages of equilibration over a cumulative contact time of 8h.

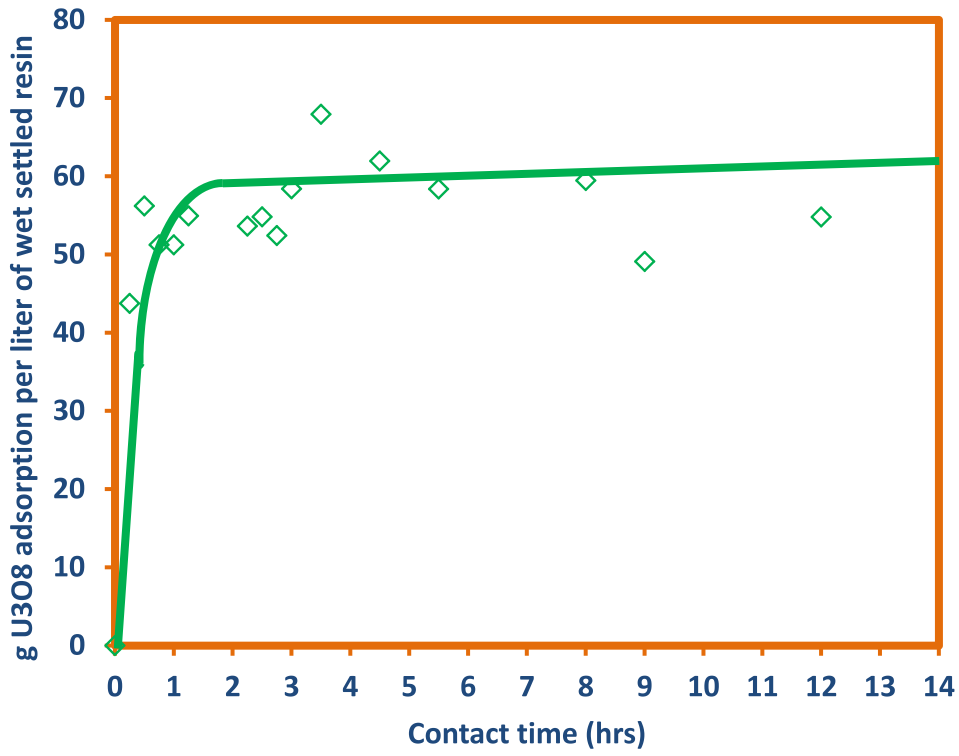
The adsorption isotherm follows Langmuir Model.



KINETICS OF LOADING FOR PFA 460/4783

The kinetics of uranium loading on PFA 460/4783 resin was determined by equilibrating 2 ml of resin with 500 ml of leach solution at ambient temperature with periodic drawl of solution samples from the reaction vessel for estimating the progress of loading or adsorption.

The kinetics of sorption of uranium was significantly fast in the initial phase, upto about 45 minutes and remained slow thereafter. About 52 g U_3O_8 /liter of w.s.r. was loaded in 45 minutes of equilibration period and reached 58-60g U_3O_8 /L of w.s.r. in 120 to 150 minutes of contact time.



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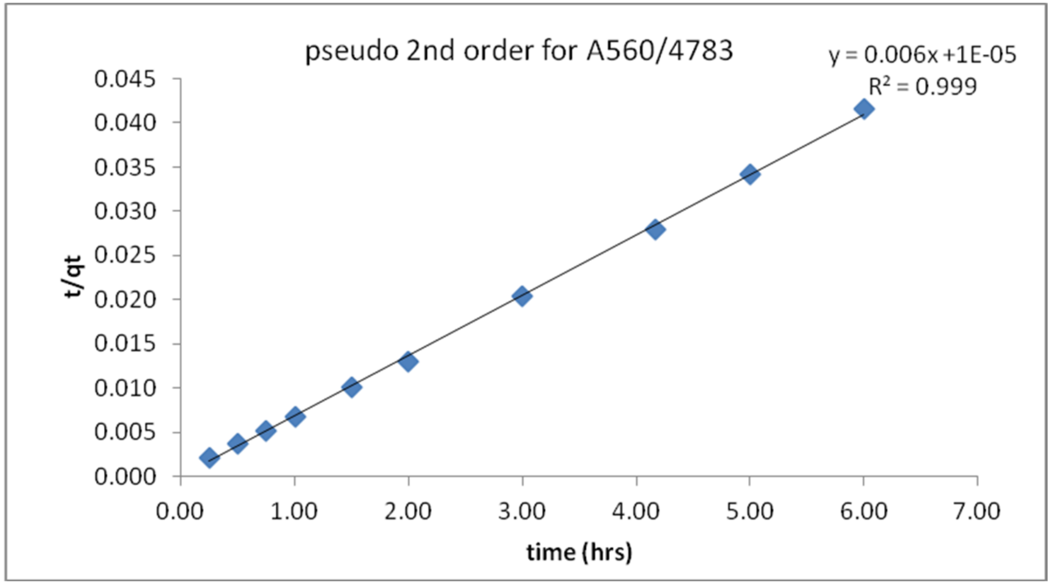


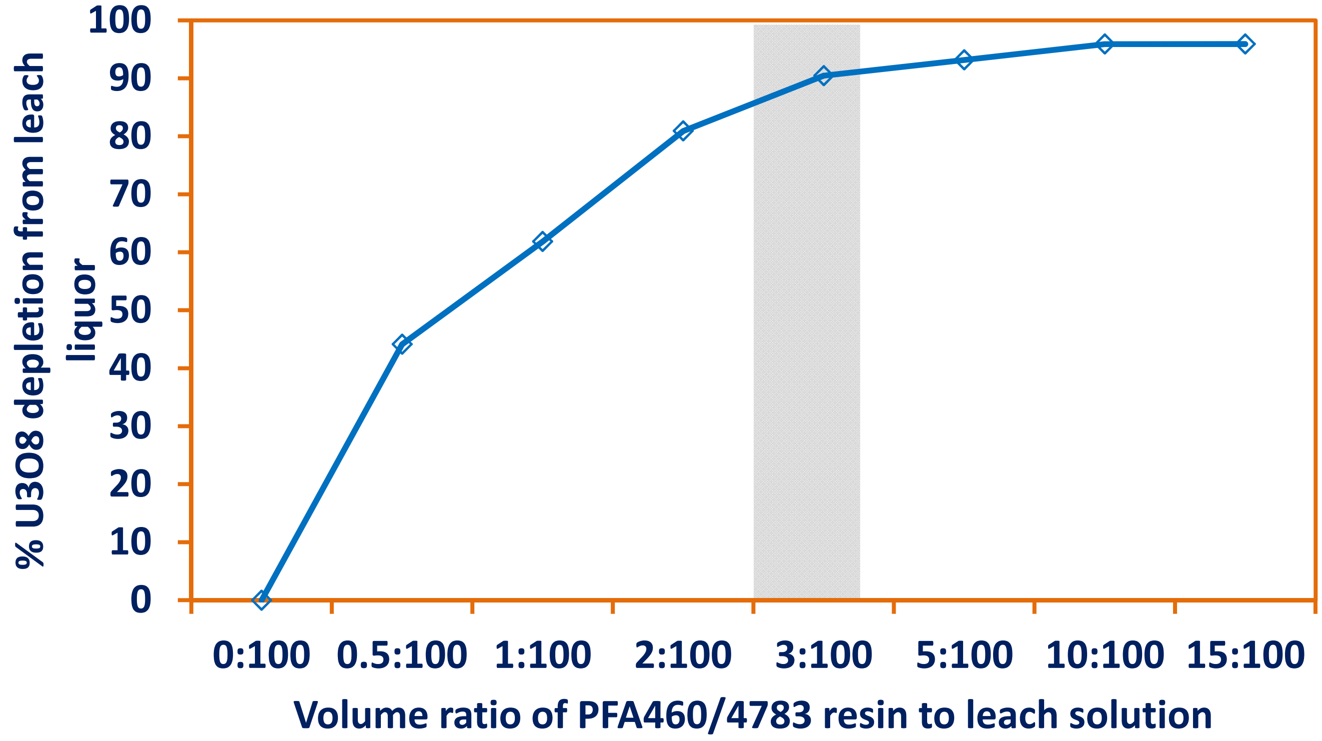
Pseudo-Second Order Rate Equation

$$t/q_t = (1/k_2 q_e^2) + t/q_e$$

where k_2 (mg/g-min) is the pseudo-second order rate constant, q_e the amount adsorbed at equilibrium and q_t is the amount of metal adsorbed at time 't'.

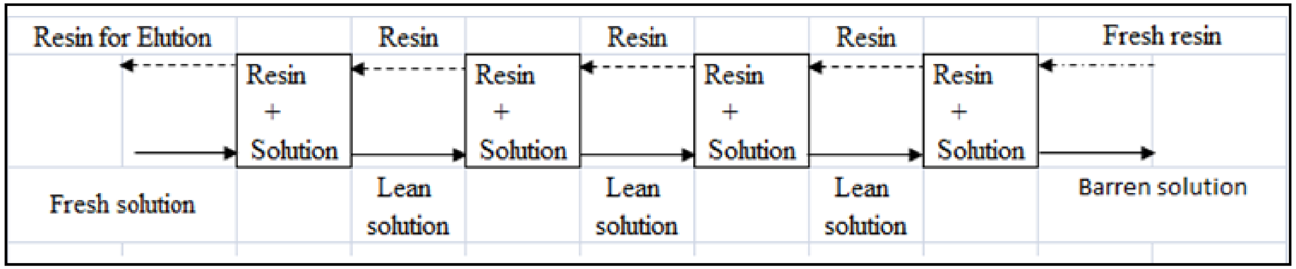
RESIN TO LEACH SOLUTION RATIO FOR PFA 460/4783

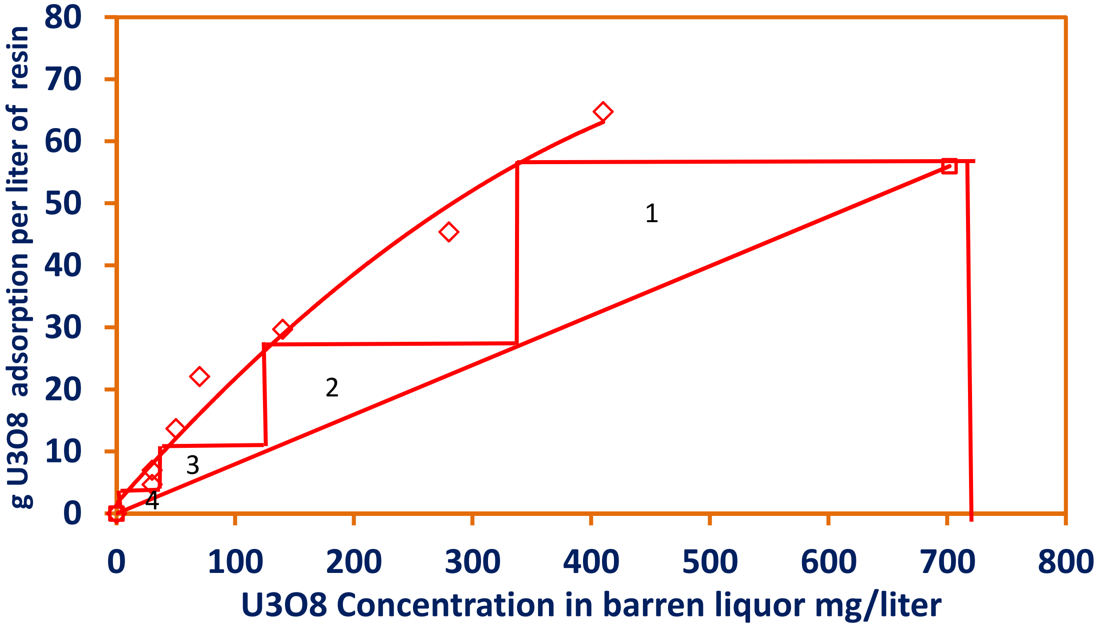
The volume of the resin was varied from 0.5 ml to 15 ml keeping the volume of leach solution fixed at 100 ml (U_3O_8 700 mg/L). The contact time in all the single-stage loading experiments was 100 minutes and the reaction was carried out at ambient temperature. The uptake was optimal (90-95%) in the ratio range of 1:33 to 1: 6.5. Single-stage extraction tests indicate resin to leach solution ratio of 1:50 to 1:33 as ideal choice for maximum loading with minimum resin inventory.



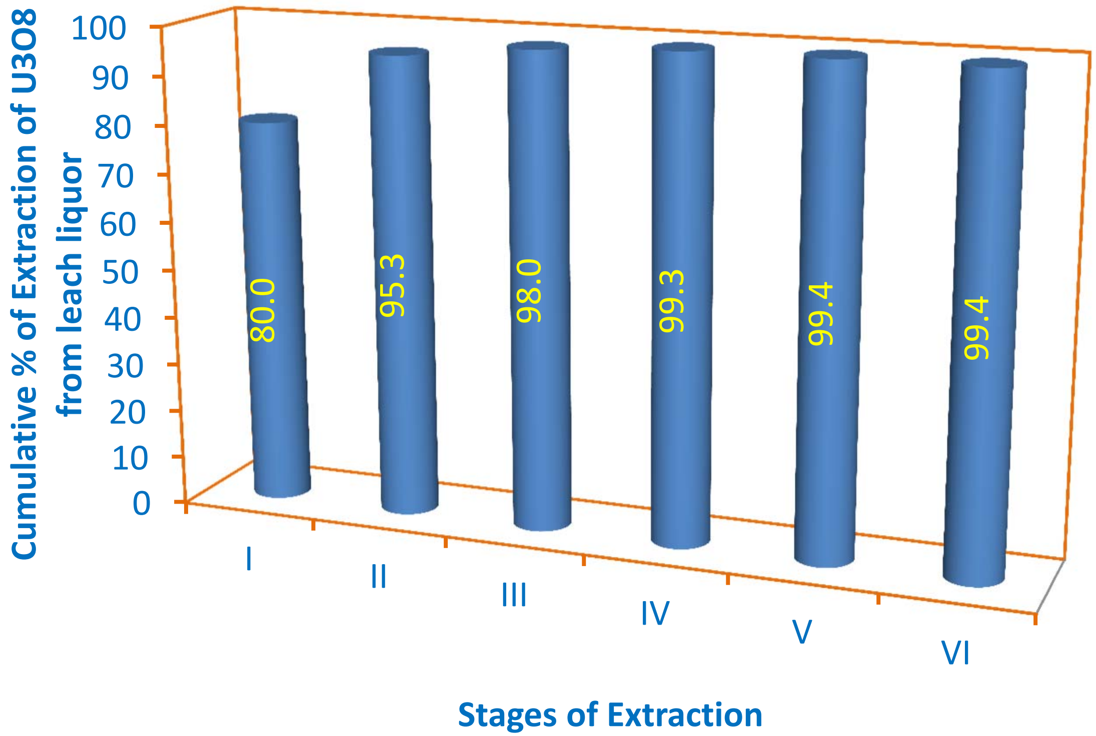
CONTINUOUS COUNTER-CURRENT OPERATION OF RIS PROCESS

The number of theoretical mass-transfer steps necessary for maximum loading of the resin with uranyl anions was determined from the McCabe Thiele plot constructed using the single-stage equilibrium isotherm results for resin-in-solution experiments. The working line was constructed using the following experimental data: U_3O_8 in feed solution 700 mg/L and U_3O_8 in final barren solution leaving the series of contactors 15 mg/L.





CONTINUOUS COUNTER-CURRENT OPERATION OF RIS – EXPERIMENAL RESULTS OF LOADING



CONTINUOUS COUNTER-CURRENT OPERATION OF RIS – SUMMARY OF RESULTS

Resin type	Strong Base Anionic
Porosity	50%
Solids specific gravity	2.8
pH for adsorption	9.5 – 9.8
Eh	110-115 mV
Capacity of resin for uranium	70 g / L of wet settled resin
Resin to Leach solution volume ratio	1:50
Specific gravity of leach solution	1.04
Specific gravity of pulp	1.24
Number of stages of contact	4 to 5
Contact time per stage	25-20 minutes
Total Contact time	100 minutes

RESIN-IN-PULP EXTRACTION WITH PFA460/4783 FOR ALKALINE LEACH SLURRIES

Based on the extensive "resin-in-solution" test work data generated with PFA460/4783 resin, the necessary experimental conditions for carrying out semi-continuous counter-current "resin-in-pulp" experiments were developed.

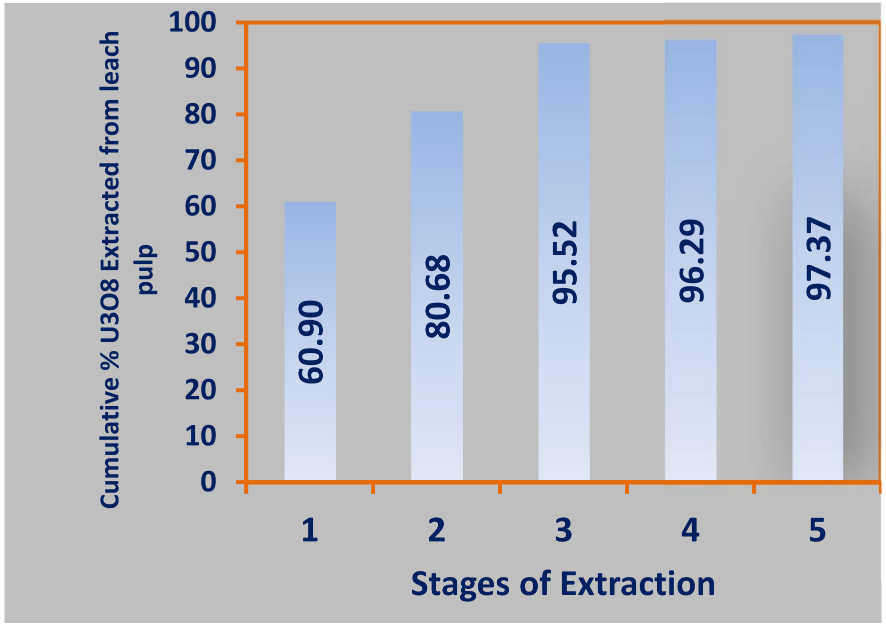
Volume of each container	900	ml
Volume resin used in each container	7.3	ml
Resin to slurry volume	0.81	%
Number of stage	5	
Pulp density of slurry	1.21	kg/l
Slurry flow-rate	4.25	l/hr
Resin flow rate	0.0345	l/hr
Peripheral speed	0.5 – 0.7	m/sec

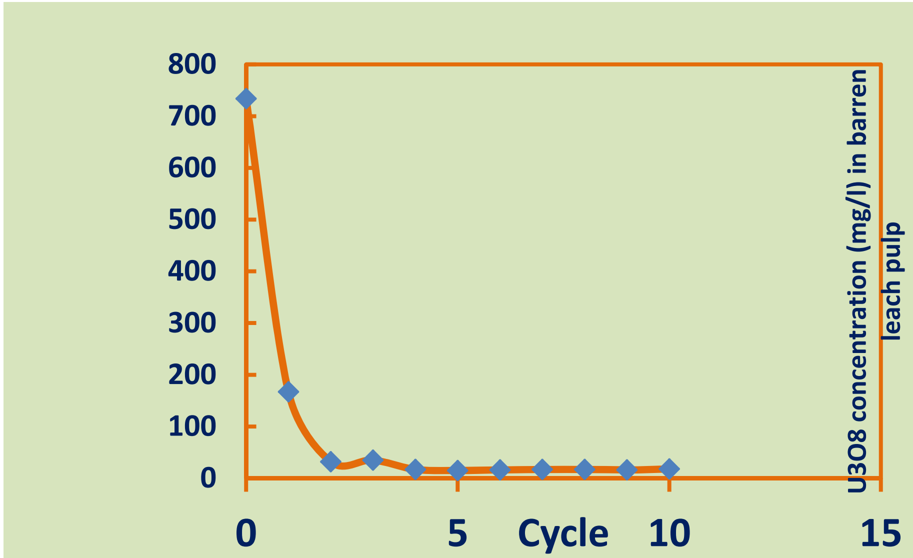
The alkaline leach slurry contained about 30% by weight leached solids. The resin-in-pulp tests were carried out at pH of about 9.5 at ambient temperature.

Resin-in-Pulp Extraction with PFA460/4783 for Alkaline Leach Slurries – Loading pattern in continuous counter-current tests

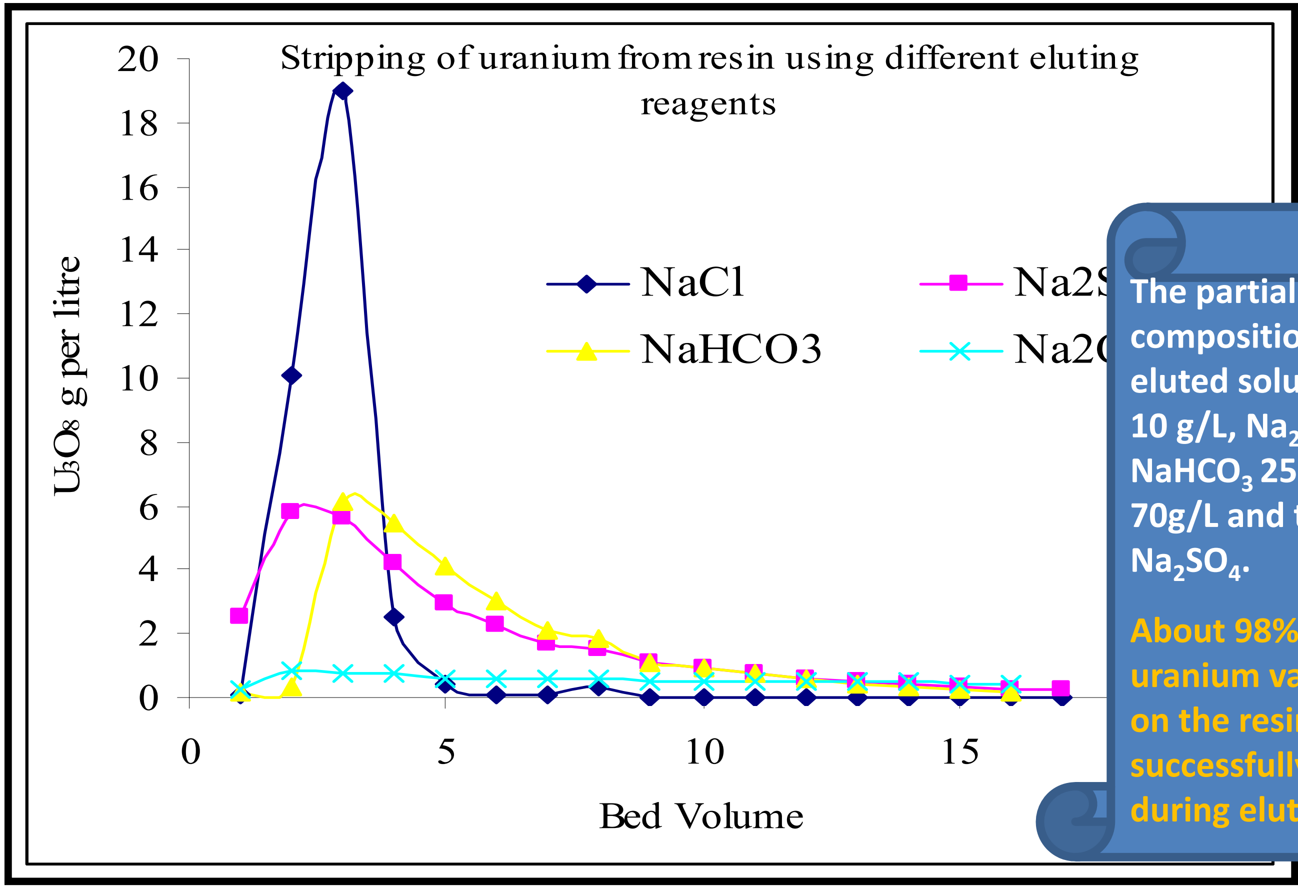
About 50 L of leach slurry was processed in the semi-continuous runs. The system attained steady state after four cycles wherein the barren solution consistently analyzed U_3O_8 content of about 15 mg/L. This works out to an extraction efficiency of about 98%.

Feed slurry chemical analysis		
U_3O8	845	mg/l
Na_2CO_3	16.7	g/l
$NaHCO_3$	19.4	g/l
Na_2SO_4	2.0	g/l
TDS	24.8	g/l





Resin-in-Pulp Extraction with PFA460/4783 for Alkaline Leach Slurries – Elution of Loaded Uranium ions



The partial chemical compositions of the eluted solution was U_3O_8 10 g/L, Na_2CO_3 3g/L, $NaHCO_3$ 25 g/L, TDS 70g/L and traces of Na_2SO_4.

About 98% of the uranium values loaded on the resin were successfully recovered during elution.

Vol. of resin:	20 ml
Eluant concentration:	1M (NaCl, Na_2SO_4, $NaHCO_3$) in 0.1 M Na_2CO_3
Elution flow rate :	2.4BV/hr or 0.8ml/min.

CONCLUSION

- Resin-in-pulp technique was applied for purification and enrichment of uranium values from a finely ground uranium ore leach slurry of alkaline nature using strong base anion exchange resin (size 500 - 675µm).

- The chemical composition of the solution phase of the alkaline leach slurry (pH 9.5) was consisting of about 40 g/L of total dissolved solutes (TDS) predominantly with Na_2CO_3 and $NaHCO_3$ and minor levels of Na_2SO_4. The uranium content was only 730 mg/L and d_{50} of solids was 34µm.

- Amongst the various commercially available resins studied PFA 4740 and 4783 having quaternary ammonium ion on polystyrene crosslink with divibyl benzez (DVB) gave best performance. The maximum loading capacity achieved in the RIP studies was about 60-65 g of U_3O_8/L of wet settled resin amounting to 98% of loading. This has necessitated 4 stages of counter-current extraction with overall contact time of 100 minutes at a resin to leach slurry volume ratio of about 1:50. Practically the entire uranium values loaded on the resin were eluted using NaCl.

- The RIP process was found quite efficient for uranium bearing alkaline leach slurries.