

Technology Development for the Alpha Decontamination of Raffinate of Metallurgical Waste by Hollow Fibre Renewable Liquid Membrane Process

C.S. Kedari

Fuel Reprocessing Division

B.K. Kharwandikar

Process Development Division

K. Banerjee

Nuclear Recycle Group

In the metallurgical waste processing facility(MWPF) a fluoride bearing, highly salted (due to Ca, Mg and Al nitrates), acidic and alpha active raffinate solution is generated. This waste solution contains residual quantity of Pu and Am. A hollow fibre renewable liquid membrane(HFRLM) process has been developed and tested with an actual 5 L raffinate solution from MWPF to diminish its alpha active nature. After treatment, the raffinate is totally depleted from Pu whereas, 37 Bq/mL alpha activity remained is due to traces of Am-241. Further evaluation for the alpha decontamination of product solution is under progress.

Introduction

Metallurgical process of Pu generates large quantity of alpha active waste in the form of slag and broken magnesium crucibles(metallurgical waste, MW). A dedicated facility (metallurgical waste processing facility, MWPF) has been created in FRD/BARC to treat this waste to facilitate its final disposal. The raffinate solution generated in the process of MWPF carries residual quantity of Pu and Am, in presence of a very high concentration of Ca, Mg and Al nitrates. Storage obligation of this alpha bearing solution is an economical liability and great concern of radiological safety. Conventional methods of separation, such as solvent extraction, ion exchange, precipitation, etc. are not economically as well as technically suitable to extract Pu and Am from such a low concentration and highly salted solutions. Liquid membrane(LM), a process intensification technology is mainly focused on the replacement of large, expensive and energy intensive equipments with that of cheaper and more efficient apparatus¹. This technology provides feasibility to combine multiple operations in a single unit². Hence, for obtaining the alpha decontamination of raffinate solution of MWPF a LM process with it's more recent configuration i.e. hollow fibre renewable liquid membrane (HFRLM) is developed. The metal ion carrier chosen for the LM process is N,N,N',N'-tetra-2-ethylhexyl diglycolamide (TEHDGA) whereas, a complexing reagent Diethylene Triamine Pentacetic Acid (DTPA) along with lactic acid(LA) are used in the receiving solution(Fig.1).

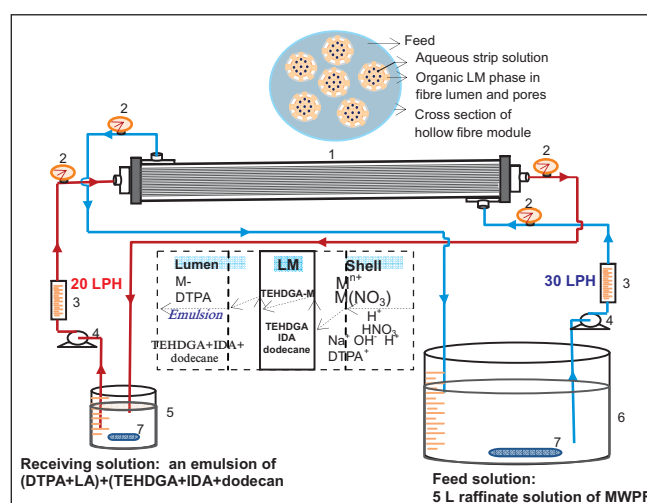


Fig.1 Schematic diagram of HFRLM process

Experimental

Reagents: Lactic acid, dodecane and DTPA and TEHDGA where procured from a local supplier. The raffinate solution was obtained from MWPF with the composition described in Table 1. Specifications of Hollow fibre membrane support are given in Table 2.

Procedures: All HFRLM experiments were carried out in a glove box. Indigenously assembled membrane system(Fig.2), equipped with two pumps, pressure gauges, rotameters and hollow fibre membrane module was used. Feed (a raffinate solution) was kept re-circulating through shell side of the membrane module where as an emulsion of strip solution with organic extractant was flowed in closed loop through the lumen side of the hollow fibres. About 0.2 bar higher pressure

Table 1: Composition of the raffinate solution(5 L) received from MWPF (before and after HFRLM treatment)

MWPF Raffinate	[HNO ₃],	[Am],	[Pu],	[Th],	¹³⁷ Cs	[Al],	[Ca],	[Mg],
	M	mg/L	mg/L	mg/L	μCi/L	g/L	g/L	g/L
Initial	1.2	1.8	2.57	235	44.8	21.3	6.27	16.8
After Cycle I	0.55	15.59 [*] (115) ^{**}	BDL	BDL	44.8	20.5	5.62	16.8
After Cycle II	0.35	0.010 [*] (180000) ^{**}	BDL	BDL	44.3	20.4	4.30	16.0

^{*}, values are in unit μg/L, ^{**}, values given in parenthesis are the decontamination factors

Table 2: Specifications of hollow fibre module used

Module reference	Liqui-cel extra flow 2.5 × 8
Porosity of the membrane	40%
Material of the fibres	Polypropylene
Number of fibres	10,000
Membrane contact area	1.4 m ²
Membrane thickness	40 μm
Priming Volumes	Shell side – 300 mL and Tube side – 200 mL (included volume of connecting tubes)

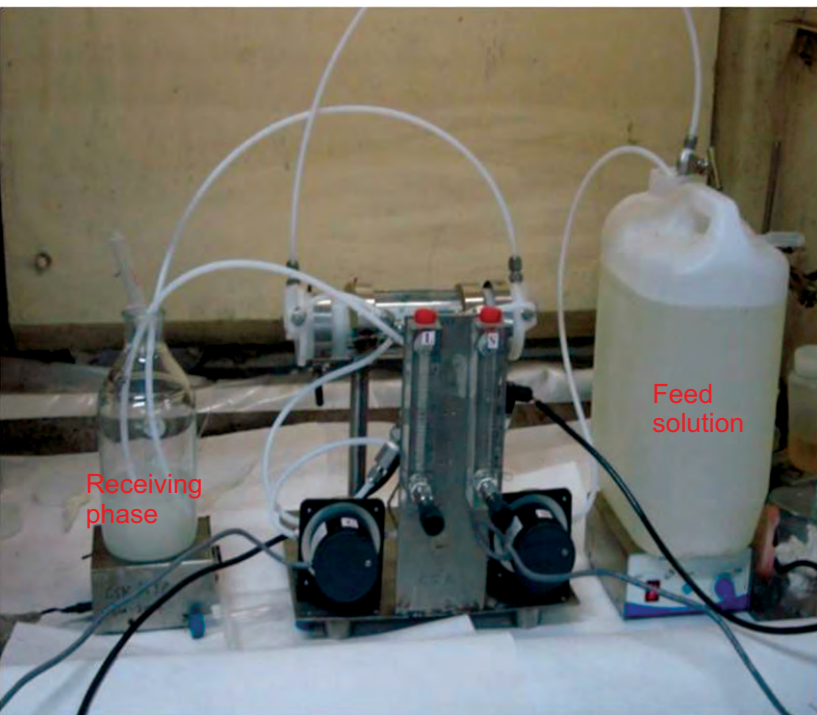


Fig.2: Hollow Fibre Renewable Liquid Membrane equipment with process solutions

was always maintained at shell side of the membrane module to restrict entrainment of organic phase to the feed solution. Samples were withdrawn from both feed and receiving solutions at fixed intervals. The pH of the aqueous part of receiving phase was monitored and maintained >3 by the addition of NaOH pallets. Concentration of Pu and Am were determined by alpha and gamma radiometry respectively. All other metal ions were determined by ICP-OES Spectrometer. The pH in the aqueous solution was measured by Metrohm 692 pH/ion meter.

The permeability coefficient, K_f of Am was obtained graphically using equation

$$\ln \frac{[Am]_{F,t}}{[Am]_{F,0}} = - \frac{K_f \times A \times t}{V_F} \quad 1$$

The concentrations of Am in the feed solution at 0 and t hours are represented by $[Am]_{F,0}$ and $[Am]_{F,t}$ respectively. A and V_F are effective area of the membrane and volume of feed solution respectively.

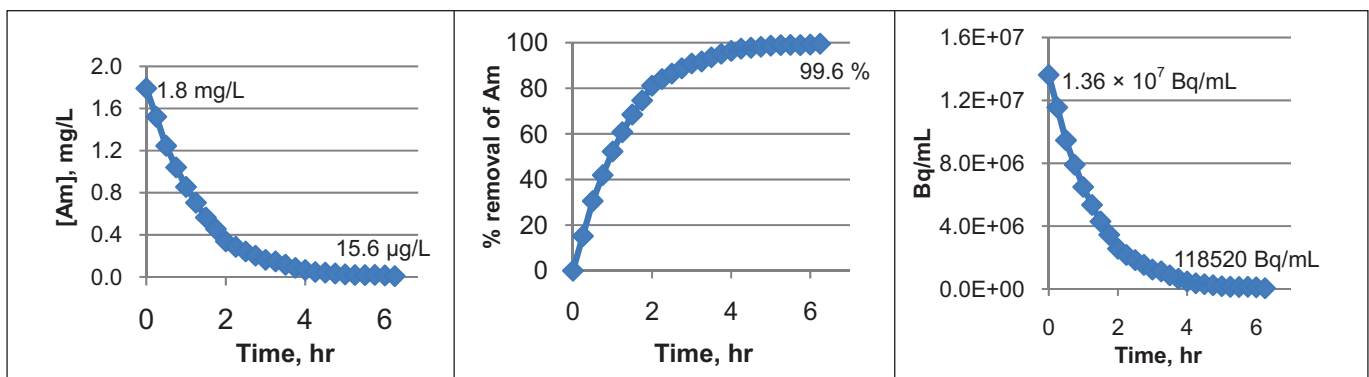


Fig. 3: Concentration profile of feed solution on time scale for cycle I

Fig. 4: Concentration profile of feed solution on time scale for cycle II

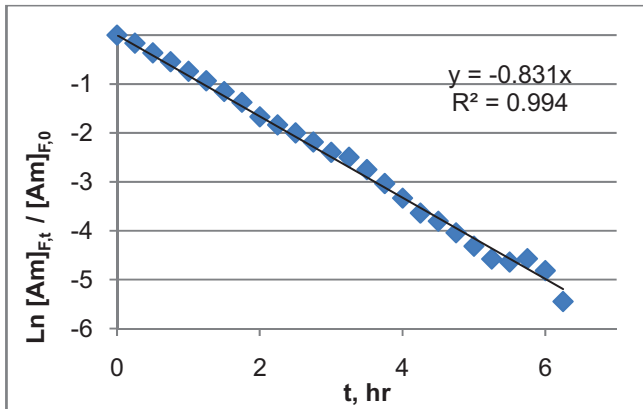
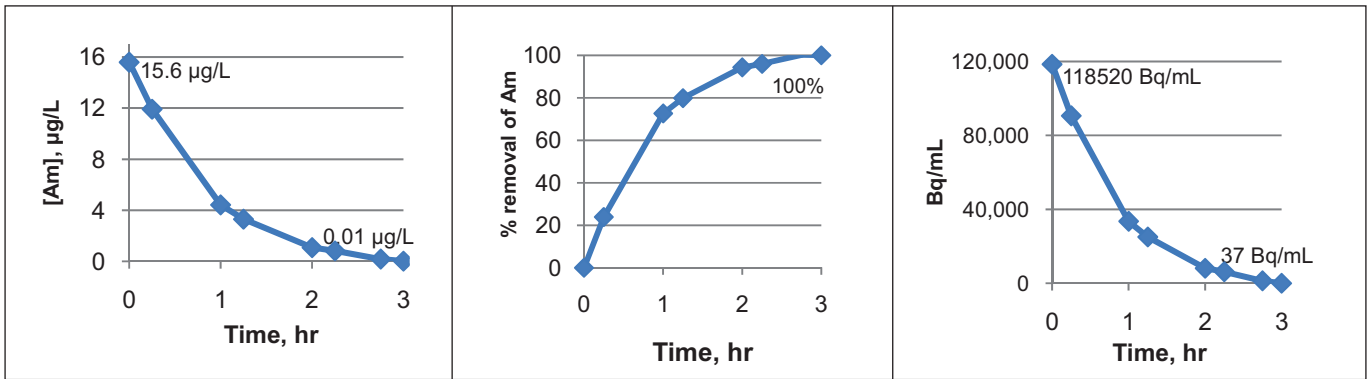


Fig. 5: Graph of $\text{Ln } [Am]_{F,t} / [Am]_{F,0}$ versus process time

Results and discussion

An actual raffinate solution from MWPF of volume 5 L is treated with optimized process of HFRLM containing TEHDGA+IDA dissolved in dodecane as LM phase supported on hollow fibre membranes. Chemical assay of raffinate solution after its treatment by the HFRLM process is described in Table 1. After I Cycle, the raffinate solution remains with 15.6 µg/L of Am, and the concentrations of Pu and Th are below detection limit. The profile of feed solution on time scale, during the HFRLM process, in terms of concentration, percentage removal of Am and alpha activity is depicted in Fig.3. The transport of Pu and Th across the

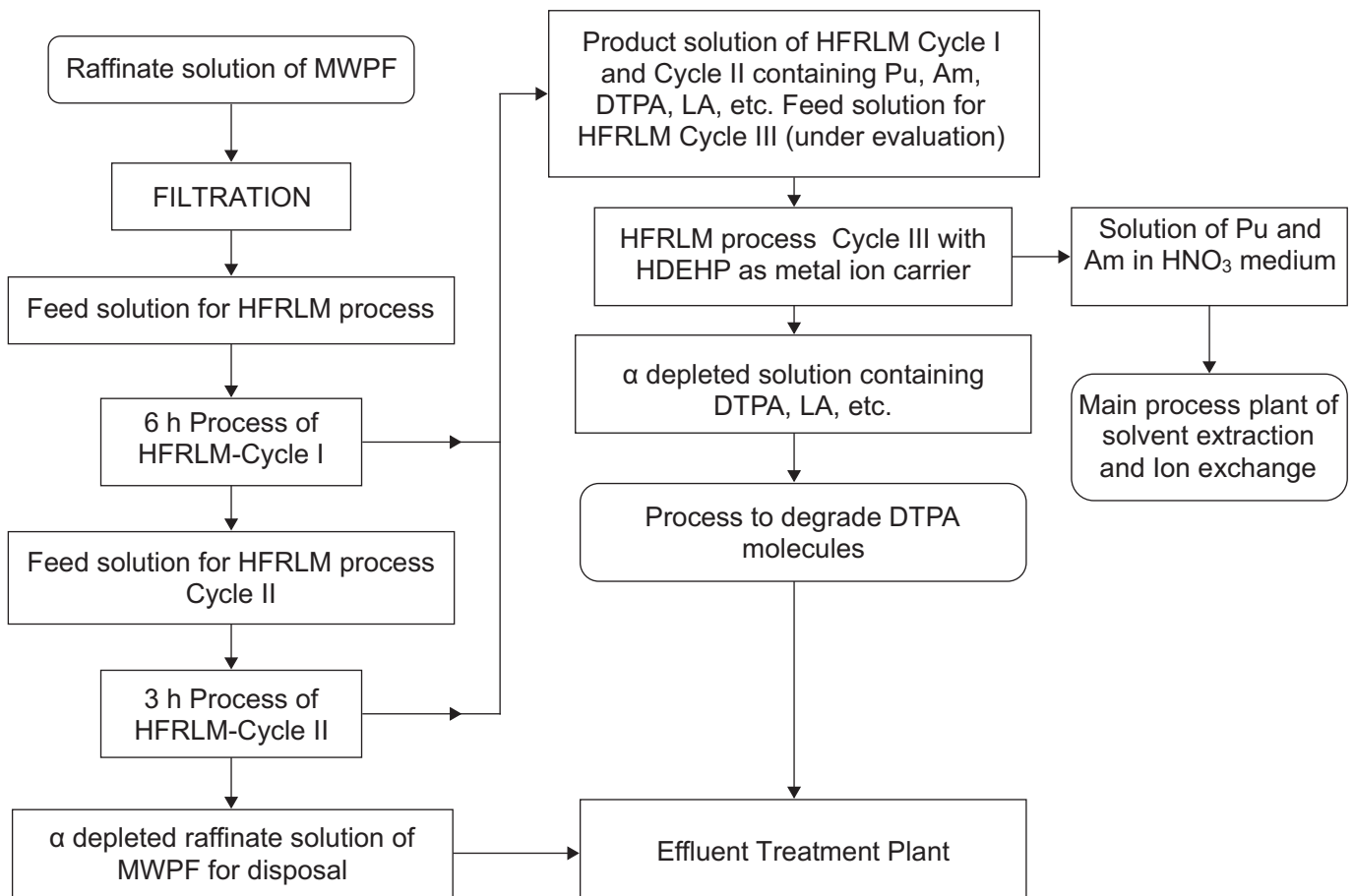


Fig. 6: Proposed process scheme for the alpha decontamination of raffinate solution of MWPF

HFRLM is faster than Am. After 6 hours of the process, more than 99% of Am is removed from the feed solution. The decontamination factor with respect to Am (df_{Am}) at this stage is 115. To obtain an alpha decontamination (a complete removal of Am) of the raffinate, it is imperative to extend the HFRLM process. In the II cycle, after 3 hours of operation, the alpha activity of feed solution came down to 37 Bq/mL ($df_{Am}=180000$). Process performance of II cycle is shown in Fig.4. Besides Th, Pu and Am, this waste solution also contains less harmful Cs-137. This HFRLM process is not separating Cs-137 whereas certain quantity of Ca is getting extracted from the feed solution. The total salt content in terms of Ca, Mg and Al nitrates, remained in feed is 97% and 93% of its initial concentration, after cycle I and II respectively. This shows a selective transfer of Th, Pu and Am with a very less quantity of other metal salts to the receiving phase. Referring to the slope obtained in Fig.5, the permeability coefficient K_f is calculated as 4.95×10^{-5} cm/min. Using K_f , time require to process the raffinate with a given concentration of Am can be predicted. Optimized conditions for the extraction of Am and Pu from the product solution of cycle I and II containing Th, Pu, Am, Ca, DTPA

and LA using separate HFRLM process are worked out. Based on this a complete scheme for the alpha decontamination of raffinate solution from MWPF is prepared and shown in Fig.6.

Conclusion

The HFRLM process developed in this work can be effectively utilized for the alpha decontamination of raffinate solution of MWPF with all of its advantages over conventional processes of separations. This process is ready for its plant scale deployment.

Aknowledgement

We are thankful to instrumentation, maintenance and operation staff of PP/FRD, for their help during this work.

References

1. Enrico Drioli, Andrzej. Stankiewicz, Francesca Macedonio, Membrane engineering in process intensification—An overview, Journal of Membrane Science 380(2011) 1– 8.
2. M.F. San Román, E. Bringas, R. Ibañez, I. Ortiz, Liquid membrane technology: fundamentals and review of its applications, J. Chem. Technol. Biotechnol. 85(2010) 2–10.