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Original Article

'Brine Management through brine mining of trace metals' for developing Secondary sources of nuclear fuel

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ABSTRACT

The brine and seawater are important and largely untapped sources of critical trace metals and elements. The coupling of selective recovery of trace metals from seawater/brine with desalination plants gives an added advantage of energy credits to desalination plants and as well as reduce the cost of desalinated water. In this paper, status review on recovery of important trace metals and other alkali metals from seawater is presented. The potential of Indian desalination plants for recovery of trace metals, based on recovery ratio of 0.35 is also highlighted. Studies carried out by the process based on adsorption using Radiation Induced Grafted (RIG) polymeric adsorbents and then fractional elutions are presented. The fouling factors due to bio fouling and dirt fouling have been estimated for various locations of interest through field trails. The pay loader in the form of compact Contactor Assembly with minimum pressure drop, for loading specially designed radiation grafted sorbent in leaflet form has been briefed, as required for plant scale facility. The typical conceptual process design details of farm assembly of project CRUDE are described.

1. Introduction

Thermal and membrane based desalination plants are being operated all over the world to address the demand of fresh water required by industries and large cities in water scarce coastal areas. The desalination and energy are very much interlinked, as plants are energy intensive. The energy consumption of desalination plants varies from 5 to 15 kWh m^{-3} of product water depending on the technology. In addition, the percentage of reject seawater/brine exiting the plants varies from 60% to 80% depending on the desalination technique adopted. The reject brine is a source of valuable trace elements/metals, which is an untapped source that is wasted. Across the globe, around 16000 plants are operating and they generate 142 million cu.m/day of brine and 95 million cu.m/day of product water. With advances in Desalination technologies, it has been established that recovery of critical technology metals and their selective recovery from reject brine of desalination plants gives an added advantage of energy credits to desalination plants as well as reduce cost of desalinated water [1,2]. Uranium and Vanadium principally exists in the form of $UO_2\,(CO_3)_3{}^{-4}$ and $VO_2\,(OH)_3^{-2}$ respectively at the prevailing pH conditions and are anionic co-ordination compounds with high solubility. Research and technological developments are required for 'brine mining' from desalination plants, i.e., by the recovery of nuclear fuel and other valuable materials (e.g. U & Li), from reject brine streams. Researchers are taking renewed interest in the development of technology for extraction of valuable species from seawater/brine, which is of ultra low concentrations [3to12]. This is being achieved by adsorption of these elements/ions onto a selective sorbent that is dipped either in reject brine/inlet seawater or in the open sea [13]. The major factor determining the practical utilization of the technology and lifetime of the radiation grafted sorbent is fouling of the adsorbent by suspended particles or due to biological growth.

Among trace alkali metals, lithium demand is around 5000 tonnes per year. It is important material in secondary batteries used in electronic gadgets. This is also being used in next generation nuclear fusion power reactor development. When lithium is an option and used in the thermonuclear plant to control thermonuclear fusion reactor the lithium requisite is around 5,00,000 t. The estimated terrestrial resources for lithium are 14 million tones [14,15]. Seawater with lithium concentration of 170 ppb and potential of 230 billion tonnes can be immense source. Nowadays, an

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Table-1
Potential of Nuclear fuel from various desalination plants in India (kg/year).

sl.no	Place	Capacity of plant (MLD)	Process	Supplier	Uranium potential (kg/year)	Li (kg/year)
1	Reliance Jamnagar	63	MED	IDE ISRAEL	242.55	11169
2	Sanghi Kutch	2.2	MED	L&T/SIDEM	8.47	390.02
3	EID-Parry Chennai	1.5	MED	IDE ISRAEL	5.775	265.92
4	NDDP Kalpakkam	6.3	Hybrid (MSF + RO)	BARC	24.255	1116.9
5a	NPCIL Kodankulam	7.5	MVC	IDE ISRAEL	28.875	1329.64
5b	do	2*1.2	SWRO	Doshi ion	9.24	425.48
6	TWAD Chennai	3.8	SWRO	BHEL	14.63	673.68
7	GEB Sikka	4	SWRO	Ion Exchange	15.4	709.14
8	CMWSSB Chennai	100	SWRO	IVRCL/BEFESA, Spain	385	17728.57
9	CPCL Chennai	26	SWRO	Ion Exchange	100.1	4609.42
				Total	834.295	38417.81

estimated 15,906 desalination plants are currently operational, located in 177 countries and territories across all the major world regions. Bardi et al. [16] estimates and suggest that by 2030 as much as 345 million cubic metres of desalinated water could be produced per day. Using this conservative figure a total of around 23,000 tonnes of lithium could be extracted per year worth around $34 million. Mentions patented process for extracting lithium ion from brine that uses electrodes made of a form of nanoscale crystalline manganese dioxide. These and other developments will improve the efficiency of brine mining and will lead to lower costs. Kang-Sup Chunga et al. [17] studied using polymeric membrane reservoir system which contains inorganic ion-exchange adsorbent inside for the recovery of lithium from natural seawater. Manganese oxide particles having high selectivity toward lithium adsorption was used as inorganic ion-exchange adsorbent. Polymeric membrane reservoir was prepared from non-woven fabric, polysulfone (PSf) membrane, PSf/non-woven fabric composite membrane, and Kimtex®. Leakage of the inorganic particles and morphology of the membrane were investigated and availability as membrane reservoir for the lithium recovery was evaluated by the lithium desorption from $Li_{1.33}Mn_{1.67}O_4$ in the membrane reservoir. The proposed system has the advantage of direct application in the sea without using pressurized flow system.

In India feasibility studies for large scale desalination plants are being carried out by many public and private enterprises to meet the future needs. The uranium and lithium potential of various desalination plants in India, at recovery ratio of 0.35 are as presented in Table-1 [2,18].

The paper presents the brine mining aspects for recovery of trace metals and other alkali metals from seawater and highlights the potential of Indian desalination plants for the recovery of trace metals. The adsorption studies carried out using radiation grafted polymeric adsorbents are discussed in this paper. The studies involve determining fouling tendency of the adsorbents in a different environment, and recovery of uranium and vanadium from the reject brine of commercial desalination plants of Indian scenario. The paper also gives the schematic diagram and major unit operations involved in process flow scheme for plant scale facility.

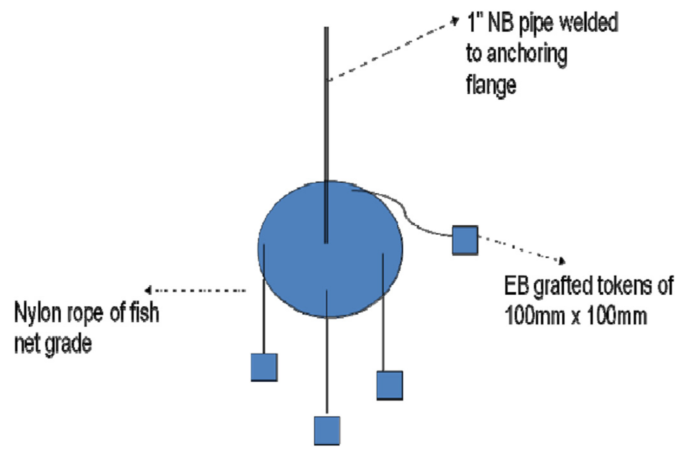

Fig. 2. Mooring set up for lab scale trials at SWRO plant Kalpakkam

2. Materials and methods

2.1. Reagents

Most of the reagents used were analytical grade for lab-scale studies and commercial grade for bench-scale studies. The chemicals were used without any further purification. Uranyl nitrate solutions of different concentrations required for lab-scale studies were prepared by a stock solution of concentration 500 ppb using low TDS water of desalination plants. Caustic flakes were used for pH adjustment of oximation and alkalination solutions.

2.2. Manufacture of Radiation Induced Grafted (RIG) adsorbent

Initial radiation grafting experiments were carried out using different types of fibers with varying cross-sections, geometry and with polymeric materials, such as polystyrene (PS) and polypropylene (PP). Based on preliminary studies, experiments were

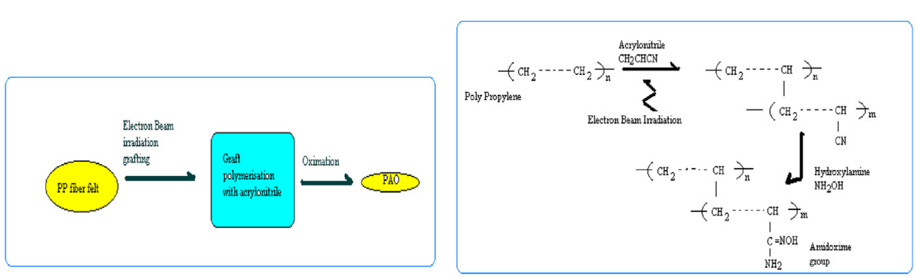

Fig. 1. Electron Beam Radiation Induced Grafting (RIG) of acrylonitrile and conversion into amidoxime group.

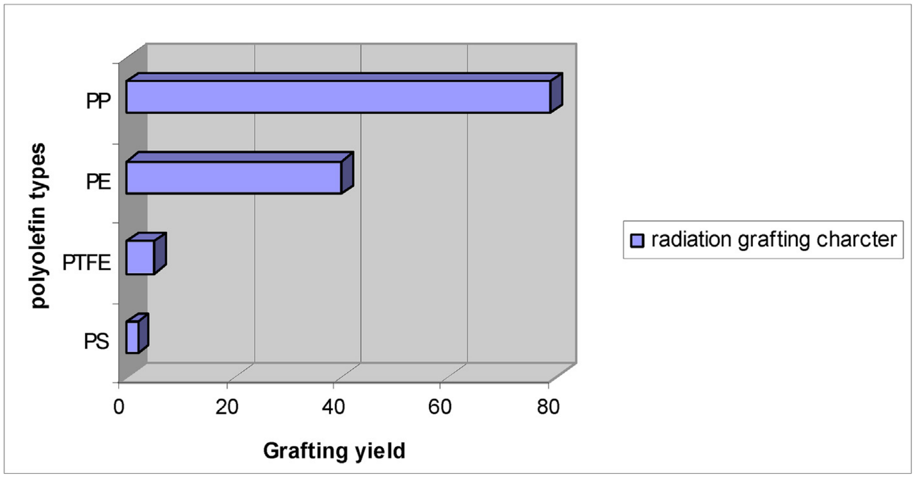

Fig. 3. Radiation grafting characteristics of various polymeric substrates.

carried out using polypropylene fiber of 1.5 denier cross section in non-woven felt form, as stem material. The optimization of the grafting of acrylonitrile on PP fiber was carried out using Electron Beam Radiation (EBR) to maximize the percentage grafting. The grafting level achieved was 110%. Subsequently, the conversion of grafted acrylonitrile into amidoxime was carried out as shown in Fig. 1.

2.2.1. Grafting procedure

Grafting reaction was carried out using a post irradiation grafting technique i.e. sheets were irradiated prior to immersing them in grafting solution. The electron beam irradiated substrate sheets were immersed in solution mixture of acrylonitrile and DMF in 70:30 ratio at 55 to 60° C for 3–4 h. Subsequently the cross-linked cyano groups were substituted with amidoxime groups. The quality assurance for grafting yield was done gravimetrically using the equation:

$$Grafting\% = \left(\left(W_g - W_i\right) / W_i\right) \times 100 \tag{1}$$

Where W_i, W_g are the weights of the sample before and after grafting.

2.2.2. Irradiation

Irradiation of substrate sheets was carried out using departmental and private electron beam accelerators under the following conditions:

For ILU-6 accelerators.

Beam energy of 2.0 MeV, current of 1.06 mA and variable conveyor speed.

For DC accelerator.

Beam energy of 1.25 MeV and 3 MeV, current = 1.0 mA and variable roller speed.

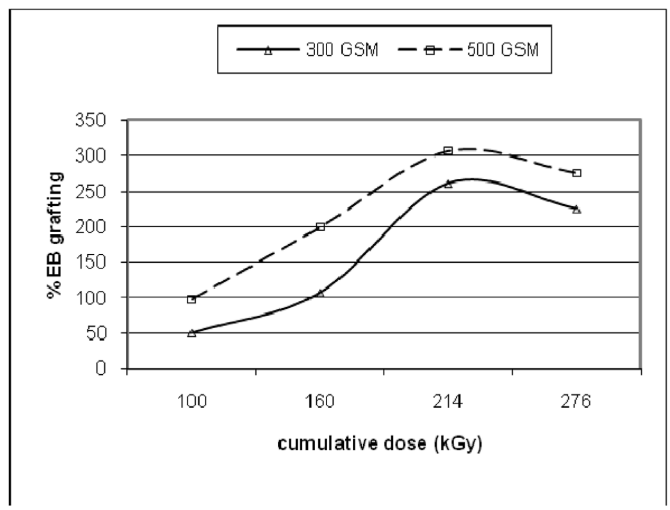

Fig. 5. Effect of radiation dose on grafting yield.

2.3. Fouling and adsorption studies

Fouling studies were carried out by immersion of radiation-

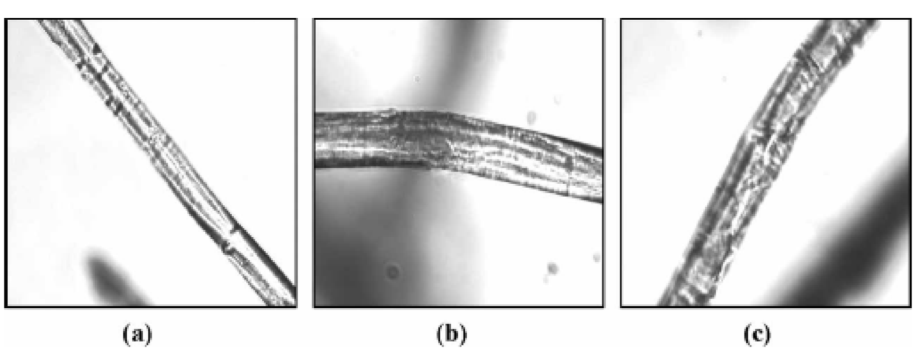

Fig. 4. Optical micrograph of a) virgin fiber b) PAN grafted fiber c) oximated PAO fiber.

Table-2
Elemental composition of irradiated and grafted substrate sheets.

Elemental composition in %	Fabric GSM	300	3PP-255-3H	500	5PPSC-48-4H	5PPSC-49-3H
	3PP-252-V	3PP-252-1H		5PP-48-V		
Carbon	87.56	73.58	71.01	88.15	70.73	70.98
Hydrogen	10.38	9.14	11.25	9.32	8.24	8.36
Nitrogen	0.07	17.27	17.65	0.12	18.59	17.85
Sulphur	0	0	0	0	0	0
Oxygen (by difference)	1.99	0.01	0.09	2.41	2.44	2.81

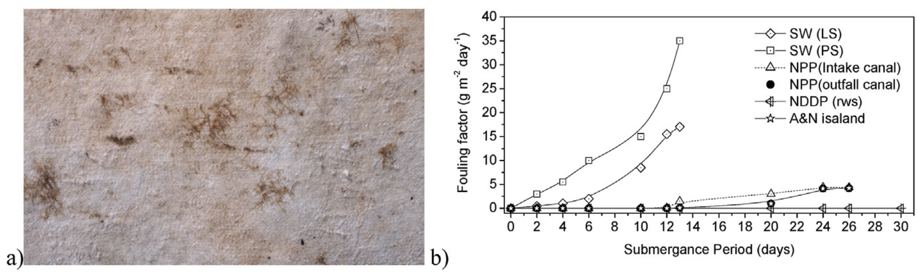

Fig. 6. *a: Nature of Dirt and Bio fouling on adsorbent sheets during field trials 6b: Variation of fouling factor as a function of submergance period at various locations (NPP: Nuclear Power Plant; NDDP: Nuclear Desalination and Demonstration Plant; SW (LS) Seawater Lab Scale; SW (PS) Seawater Plant Scale; A&N(Andaman and Nicobar)islands.*

grafted adsorbent in different locations such as seawater in the lab and in actual location as well as inlet and outlet of commercial scale desalination plants. The mooring set up arrangement for dipping the tokens are as shown in Fig. 2. The uranium and vanadium recovery from Sea Water Reverse Osmosis (SWRO) plant is fractionally eluted and estimated and the results are presented.

3. Results and discussions

3.1. Radiation characteristics of various polymeric substrates

In our studies, we have used non-woven thermally bonded materials as substrate materials. Non woven materials are porous media consisting of fibers or filaments oriented mainly in the x,y directions according to the method of fabric production. The fiber size and filament type has significant influence on the geometrical, hydraulic and mechanical properties of the fabric. The pore size distribution of nonwovens is particularly important in respect of transport phenomena within the structure. Four types of polymers polystyrene, poly tetra fluoro ethylene, polyethylene, and polypropylene were used as sample substrates to investigate radiation-grafting characteristics of polyolefin. Among the samples tried, polystyrene shows most radiation resistant since absorbed energy converts into heat by aromatic rings. Radiation processing is limited and radiation yield of radicals is limited than in other polymers. Three radicals can be produced - two are formed on abstraction of hydrogen and one created via addition of hydrogen to aromatic ring. In case of PP, the dominant product is 3rd order alkyl radical that undergoes oxidation. Formed peroxy radicals are very stable. PE is also radiation resistant polymer, but ionising radiation induces residual radicals in crystalline phase. The alkyl, allyl and polyenyl radicals are produced. The Fig. 3 shows the radiation grafting yields

Table 3
Uranium and Vanadium pick up assessment at Sea Water Reverse Osmosis (SWRO) brine stream NDDP Kalpakkam

Sl. No.	Parameters	Poly (Amidoxime) (PAO) token 2	Poly (Amidoxime) (PAO) token 6
1	Substrate		
	a. Size (mm)	a. 110 × 70	a. 120 × 75
	b. Weight (g)	b. 6.7	b. 9
2	% grafting	110	110
3	In situ Alkalination		
	a. Concentration	a. 5% NaOH	a. 5% NaOH
	b. Duration	b. 2 hrs	b. 2 hrs
4	Submergence		
	a. Location	a. RO-Reject Water Sump (SW direction.)	a. RO-Clarifier Water Tank (NE direction)
	b. Duration	b. 360 hrs	b. 360 hrs
5	Elution for Uranium/Vanadium		
	a. Temperature (C)	a. 60	a. 60
	b. Time (hr)	b. 4	b. 4
	c. Eluent	c. 0.5 M/5M HCl	c. 0.5 M/5M HCl
6	Analysis of elute*		
	a. Uranium	a. 339 ppb	a. 393 ppb
	b. Vanadium	b. 37.8 ppb	b. 41.6 ppb
7	Concentration factors observed		
	c. Uranium	c. ~100	c. ~120
	d. Vanadium	d. ~19	d. ~20

* As reported by AChD, BARC.

Table-4
Typical process design details for Project CRUDE (Coupling of Recovery of Uranium from Desalination Effluent).

Sl.no	Item details	Quantity	Conceptual details
1	Radiation grafted PAO sorbent	3 tonnes	Loading factor of 0.1 g/kg PAO/ cycle
2	Stem material	5 tonnes	300 gsm non woven sheets
3	No of Contactor assemblies	30	16 Modules of 1m × 1m x 1m in one CA
4	No of units to be handled per day	3	
5	Life of substrate	20 cycles	
6	Total cycle time	20 days	Around 15 days of submergence in mooring canals

observed for various substrate polymers. The changes occurred due to irradiation, grafting and oximation are characterized by optical micrographs and scanning electron microscope for the purpose of characterization of changes in structure and morphology. Fig. 4 shows changes both in texture and diameter of the fibers.

3.2. Parametric studies on irradiation and grafting of substrate sheets

The radiation processing by electron beam technology has been adopted in the present work for developing polymeric adsorbents through the process of radiation grafting. Compared to the chemical processing that induces the same type of reaction, EB processing induces direct electron-to-electron interactions. Three standard methods of grafting developed were Mutual grafting (simultaneous) method; Pre irradiation (consecutive) method and Peroxide methods. In the present work, the combinations of these methods have been used to develop post irradiation grafting technique to increase the radiation grafting yields. Free radicals have been chosen almost exclusively as the reactive intermediates. Heterogeneous process consists of backbone polymer in solid form such as fiber and the grafting monomer in liquid form. Here the polymer is irradiated in the presence of air to produce mainly hydro peroxides. These polymer oxides, which are often quite stable, can be decomposed in contact with monomer to produce graft co-polymers (grafting process as explained in earlier paper [19]). Solvents are used to increase the monomer diffusion and enhance the efficiency and uniformity of the grafting. The electron beam energy of 3MeV was used for carrying of grafting trials. Fig. 5 shows the grafting yields as a function of the cumulative dose at a dose rate of 10 MRad/pass in air and reaction was carried out at 60 deg.C for 3 h. The yields are increased with the dose up to ~200 kGy and then leveling off is observed for substrates of different densities. The elemental composition of virgin and grafted sheets were analysed and are as shown in Table-2. Increased nitrogen composition is observed in grafted samples.

3.3. Fouling factors assessment of various submergence conditions

The seawater/brine is bio aggressive multi component feed. The feed solution conditions and fouling conditions have an effect on

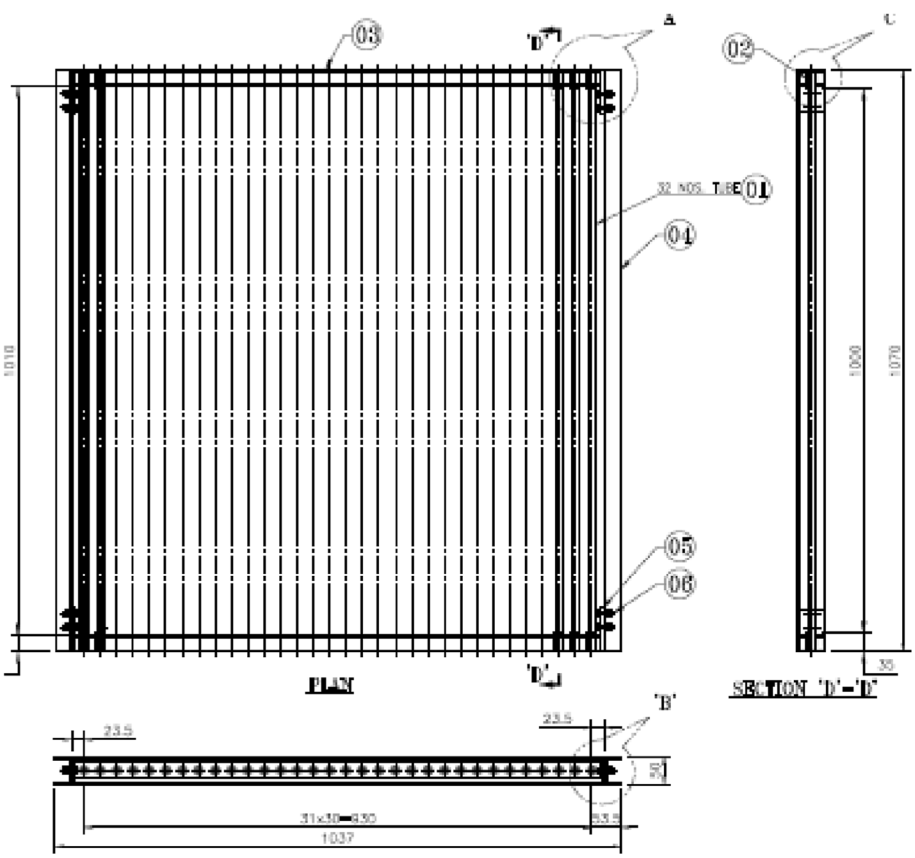

Fig. 7. Plan and Elevation of module (CA111) of titanium assembly.

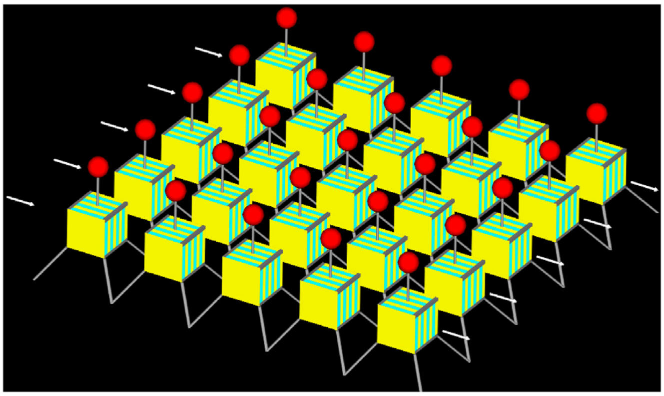

Fig. 8. Conceptual schematic of farm assembly for 5 × 5 modules.

the adsorptive properties of radiation-grafted adsorbents. In case of uranium recovery from seawater/brine, the functional groups existing on the surface layer are occupied by various kinds of metal ions and are quickly covered with dirt and bio growth. The nature of dirt and bio growth found on sorbent sheets during field trials is shown in Fig. 6a. The fouling factor assessment was carried out at various locations and is shown in Fig. 6b. The recovery of trace metals depends on diffusion in bulk, in film, intra-particle type of diffusion as well as chemical reaction steps. The fouling factors observed for nuclear power plants and desalination plant conditions are lower than the seawater conditions at high seas. The submergence period of beyond 12–13 days is possible for brine conditions due to less biofouling and dirt fouling. The fouling factors observed for nuclear desalination plants were negligible, even with extended submerged periods.

3.4. Brine mining studies at desalination plant sites

Bench-scale brine mining experiments were carried out by using Poly Amidoxime (PAO) adsorbent coupons of various sizes. These tokens are submerged in Reverse Osmosis (RO) Reject Water Sump (RWS) and Clarified Water Tanks (CWT) at NDDP Kalpakkam for a period of around 15 days to assess the feasibility of recovery of valuables from reject brine stream and the results are presented in Table 3. Elution was carried out using hydrochloric acid media at elevated temperature of 60 °C.

3.5. Coupling of recovery of Uranium and other valuables from desalination effluents (CRUDE) of desalination plants

Based on success of extracting uranium with concentration factors of more than 50 by harnessing the tidal wave and as well as flow streams of desalination effluents, using electron beam grafted amidoxime as adsorbent, the conceptual process scheme for scaled up facility ‘CRUDE’ to extract 3 kg of Uranium per annum has been developed. The substrate material of adequate strength and quality were selected based on chemical and radiation characterization of various makes used during bench scale trials. The contactor assemblies contribute almost 51% of the capital cost and its life is very critical for cost optimization. It is being planned to use titanium grade-2 as MOC, designed for tidal current of 1 m/s velocity and the same is finalized based on operating experience during first phase trials. Table-4 shows typical process design details for scaled up facility of extract 3 kg of Uranium per annum. Fig. 7 shows the various views of CA111 type module of titanium contactor assembly details required for aquaculture of trace metals from seawater/brine. The CA111 assembly facilitates loading of sorbent sheets of size 1M × 1M.

The details for ‘compact and pressure drop free’ Contactor Assembly (CA) of size 4m × 4m x 1m have been worked out to house 480 grafted sorbent sheets, as required for plant scale facility. The typical conceptual process design details of farm assembly of project CRUDE are as shown in Fig. 8 below.

4. Conclusions

The brine mining studies have given promising results for recovery of uranium and vanadium from brine/seawater and an improvement of concentration factors by two orders are observed. The study shows that the coupling of uranium recovery unit with desalination plants gives the added advantage of faster adsorption kinetics with bare minimum fouling factors for the mass transfer coefficient. The substrate with high GSM have shown field worthiness for harnessing using available pressure drops of desalination plants. The world’s desalination plant capacity is around 95 million m^3/day and whereas the desalting capacity in India is around 2.5 million m^3/day. This has potential of approximately 8 tonnes of uranium and 44 tonnes of lithium. The oceans are being the most important as well as promising resources of the lithium for the near future to meet the demand of lithium of world community. Many countries are taking renewed interest in this ambitious research programme. The fouling factor, which decides the lifetime of the adsorbent in the actual condition, is the deciding factor for the implementation of the technology at a specific location. Brine production across the world is around 142 million m3/day. The economics of desalination process will become still more attractive in future as more and more rare and strategic elements like lithium; rubidium are extracted in addition to uranium and vanadium.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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