

A Review of Uranium Extraction from Seawater: Recent International R & D

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Abstract

Radiation-induced grafting co-polymerization is widely used technique to produce high performance chemically active polymer materials for adsorption and separation processes on the basis of various commercial polymers available in different forms (films, fibers, resins, textiles, powders). The design and synthesis of polymer supported reagents that can selectively complex metal ions from multi-component solutions have been an important area of research during the last decades. Uranyl ions have been one of the target ions to be removed from aqueous systems. Despite the very low uranium concentration (3.3 ppb) in seawater, it's total amount reaches 4×10^{12} kg, that is equivalent to 1000 times of the mine uranium. To recover an economically significant quantity of uranium from seawater, an adsorption method using a suitable solid adsorbent seems to be feasible with regard to economical and environmental impacts. Extensive investigations of adsorbents capable of recovering uranium from seawater and aqueous systems have been carried out during the last two decades especially in Japan Atomic Energy Agency, Japan but until now, this method is not feasible for mass production. In this paper, recent international activities are summarized, on both the laboratory scale experiments and large scale marine experiments. R & D opportunities are discussed for improving the system performance and making the collection of uranium from seawater more economically competitive.

Keyword : radiation, grafting, uranium extraction, seawater

1.0 Introduction

The concept of recovering minerals from seawater has been proposed as a way of counteracting the gradual depletion of conventional mineral ores. Seawater contains large amounts of dissolved ions and the four most concentrated metal ones (Na, Mg, Ca, K) are being commercially extracted today [1]. However, all the other metal ions exist at much lower concentrations. Uranium has relatively low concentration (3.3 parts per billion in seawater), but the tremendous amount of uranium dissolved in the sea (more than 4×10^{12} kg) has long been regarded as a nearly inexhaustible resource [2]. The present supply of mineral uranium is only

about 60% guaranteed by mineral sources; the rest is being obtained from stockpiled uranium resources derived in large part from dismantled atomic warheads [3]. Increasing uranium production from land mines would require large investment and, eventually, the increasing energy requirement of uranium extraction from low grade ores could make the whole activity self-defeating [3,4].

Extraction of uranium from seawater was identified as one of the Fuel Cycle R & D program worldwide, which the main goal is to evaluate uranium resources and develop recovery technologies to increase its availability to enable sustainable fuel cycles. Uranium exists in the

ocean as soluble uranyl carbonate complexes, which could be extracted, without the complex and energy intensive processes of extraction and beneficiation which are typical of land mining. In addition, an important fraction of the minerals which are lost as waste at the end of the economic process end up in the sea as dissolved ions. In this sense, the oceans could be considered an infinite repository of materials that could be used for closing the industrial cycle and attain long term sustainability.

Extraction of uranium from seawater has been investigated for many years. Many government sponsored research and development (R&D) activities were carried out in the 1970s and 1980s. However, most of the studies were subsequently suspended due to low recovery efficiency and modest uranium market prices. This paper summarized recent international activities on both the laboratory scale experiments and large scale marine experiments. R & D opportunities are discussed for improving the system performance and making the collection of uranium from seawater more economically competitive.

2.0 Recent Development in Japan

Japan is one of the few nations that has high commitment in seawater extraction and maintained by far the largest research efforts. The extraction of was first studied by Japan Tobacco and Salt Corporation in 1960s. Since then, many universities and institutes have carried out laboratory experiments. In 1974, Japan Government started the program to study recovery of uranium from seawater. The earlier studies focused on evaluation of different methods such as solvent extraction, ion exchange, flotation, biomass collection, adsorption, and development of adsorbents (hydrous TiO_2 , PbS) [5]. Kanno [5] reported that hydrous TiO_2 was a promising adsorbent for the

collection of uranium from seawater, but the high pumping costs plus the low mechanical strength of the hydrous titanium oxide absorbent led the researchers to pursue investigation of the graft polymerization with amidoxime type of functional groups.

Recent studies conducted by Japanese Atomic Energy Agency (JAEA) has prepared a pre-irradiation fibrous amidoxime-based adsorbent for uranium extraction from seawater and carried out the marine experiment to evaluate the uranium collection from seawater. In 1999, a new 3-year effort was initiated to start the marine experiments of the mass produced adsorbent fabric materials. A stack design with a floating frame and cage of adsorption beds was placed about 7-kilometer offshore of Aomori, Japan.

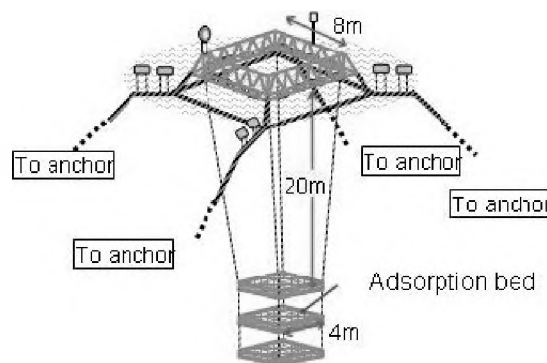


Figure 1 : Uranium collection system for adsorbent stacks [5]

The adsorption beds were suspended on a floating frame down at least 20-meter from the surface. A crane ship was used for hanging the cage of adsorption beds from the floating frame every 20-40 days. A total of 1 kg of uranium was collected as yellow cake. Dilute acid (0.5M HCl) was used to elute the sorbed uranium from the adsorbent materials. A follow-up purification by solvent extraction is required before the extracted uranium feed can be used for yellow cake production.

The costs associated with the floating frame and cage in the stack design represented ~80% of the

collection cost. Therefore, a new collection system for cost reduction by using a braid type adsorbent was developed later in the marine testing [6].

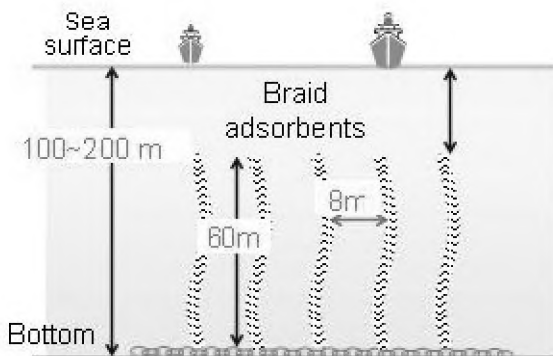


Figure 2 : Uranium collection system for braid adsorbent [5]

In this braid design, polyethylene fiber was treated by radiation process to generate the braided adsorbent materials. The 60-meter long adsorbent was evaluated in Okinawa, Japan. The braid adsorbent was moored to the sea floor with a remote control device and stood/floated in the sea currents. In this new design, the recovery of uranium using the braid adsorbent system was 1.5 g U/kg-ad versus 0.5 g U/kg-ad with the stack methods, due to the higher efficiency of the braid system than the stack system. The estimated uranium yellow cake recovery cost was 25,000 yen/kg for a 1,200 t plant design with an adsorbent lifetime of 18 adsorption/elution cycles [6].

3.0 Recent Development in India

An extensive work has been carried out by Bhabha Atomic Research Centre (BARC), Mumbai, India. The work was conducted by two groups: Radiochemistry Division and Desalination Division. The studies focused on the amidoxime based adsorbent systems, in the forms of membranes [7] or hydrogels [8]. Other systems with resin or magnetic particles grafted with ligands (such as amidoxime or calixarene)

were also studied [9]. The amidoximated macroporous membranes were prepared by post-irradiation grafting using electron beam. Meanwhile, hydrogels were prepared by cross-linking using UV-initiated bulk polymerization technique.

Under a collaborative project between BARC and Commissariat à l'Energie Atomique of France (CEA), work was conducted to extract uranium from the concentrated brine rejected by desalination plants in BARC [9,10]. An R&D program called RUSWapp (Recovery of Uranium from Sea Water pilot program) in BARC was initiated [10]. The objective of this program is to recover some of the rare and valuable elements (including uranium) from the rejected brine of the desalination plant, which helps make the desalination plant more environment-friendly and reduce the cost of desalinated water. The effluent rejected from the desalination plant contains a number of materials. Three methods have been proposed for this program : 1) Resin grafted with calixarene; 2) Magnetic separations using magnetic particles grafted with calixarene; and 3) Canal system with braid adsorbents [10].

2.3 Other countries

Activities for extracting uranium from seawater began in China during 1970's and are still active until now. However, most of the work focused on evaluating absorbents and understanding the kinetics and mechanism of absorption. Jin et al. reported that hydrous titanium oxide, aluminum hydroxide, and organic resins were among the absorbents tested in late 1970's – early 1980's, meanwhile more recent studies were evaluating polyacrylamidoxime and chitin for the extraction of uranium from seawater [11].

Although effort to develop amidoxime methods for uranium extraction from seawater has largely occurred in Japan, the first study on the

extraction of uranium from seawater was carried out by Great Britain in 1953 [12]. Research activities on the extraction of uranium from seawater from a number of European countries are also reported, including Finland, France, Germany, Greece, Italy, Poland, and Sweden.

3.0 Conclusion

In conclusion, research program for extracting uranium from seawater is on-going worldwide. Although most of it does not seem feasible enough to compete with the uranium price from

mining, there are many areas for possible improvements for it to be economically viable in the near future. Various areas needed to be explored, such as the performance of the collection systems, selectivity, loading capacity, chemical stability and mechanical durability, as well as the sorption kinetics, for further improvement. Other completely different method for harvesting the ocean's vast uranium resources is yet to be explored, but at the moment amidoxime extraction method developed by Japan appears to be very promising.

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