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Extraction of Uranium from Seawater Using Magnetic Adsorbents

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ABSTRACT

A new process for the extraction of uranium from seawater was developed. In the process, uranium adsorption is effected using powdered magnetic adsorbents; the adsorbents are then separated from seawater using magnetic separation technology. This process is superior to a column method using a granulated hydrous titanium oxide adsorber bed in the following ways: (1) a higher rate of adsorption is realized because smaller particles are used in the uranium adsorption; and (2) blocking, which is inevitable in an adsorber bed, is eliminated.

The composite hydrous titanium-iron oxide as a magnetic adsorbent having high uranium adsorption capacity and magnetization can be prepared by adding urea to a mixed solution of titanium sulfate and ferrous sulfate. Adsorption and desorption of uranium and the removal of the adsorbent using a small-scale uranium extraction plant (about 15 m^3/d) is reported, and the feasibility of uranium extraction from seawater by this process is demonstrated.

INTRODUCTION

Several methods have been proposed to recover uranium from seawater; these include adsorption (1,2), coprecipitation (3), ion flotation (4), and solvent extraction (5). Of these, adsorption is generally regarded as the most feasible technique. In this regard, the use of slurries has two major advantages over the operation of columns: (1) higher rates of adsorption and desorption can be attained by employing small particle size adsorbents; and (2) the problems attending blockage of the adsorption column are avoided.

For the recovery of uranium from seawater, however, the slurry method is limited in that the usual methods for separating the adsorbent from the seawater, viz., sedimentation or centrifugation, cannot be applied because of the amounts of seawater which must be processed. To overcome this limitation, a process called "slurry adsorption-magnetic separation" has been developed (6). In this process, a magnetic adsorbent (7) is employed in the slurry method, and the adsorbent is subsequently separated from the seawater with a high-gradient magnetic separator.

A small-scale plant, with a capacity of 15 m^3 of seawater per day and which utilizes the slurry adsorption-magnetic separation system, has been constructed and operated at the Sakaide seashore, Kagawa prefecture, in Japan. The facility was used to extract 314 mg of uranium from 292 m^3 of seawater; the overall recovery of uranium was 37%.

Although several problems remain to be solved, the new process has been found to be technically feasible for uranium extraction from seawater.

SLURRY ADSORPTION-MAGNETIC SEPARATION SYSTEM

A block diagram of the slurry adsorption-magnetic separation system for the extraction of uranium from seawater is shown in Fig. 1. The system is divided into four processes:

(1) Adsorption process

Magnetic adsorbent is added to the adsorption vessel containing seawater. The slurry is kept stirred with a vertical stirrer. In this process, the uranium in the seawater is adsorbed on the magnetic adsorbent.

(2) Magnetic separation process

After the adsorption process, the slurry is transported to and passed through a high-gradient magnetic separator (HGMS). Here the adsorbent is trapped on a filter by the magnetic force.

(3) Desorption process

The adsorbent trapped on the filter of the HGMS is processed, and uranium on the adsorbent is desorbed by an eluent, such as a carbonate solution. The concentration of uranium in the eluent is several milligrams per liter. The magnetic adsorbent is then washed and recycled to the adsorption vessel by removing the magnetic field.

(4) Secondary concentration and purification process

It is necessary to increase the uranium concentration and to eliminate impurities in the eluent. For this purpose, an ion exchange method is usually adopted. The concentration of uranium in the final eluent, such as an HCl solution, is 1,000 to 3,000 ppm. Finally, a precipitate of uranium is obtained by adding a precipitating agent in the eluent.

DESIGN OF THE SMALL SCALE PLANT

A schematic flow diagram of the small scale plant is shown in Fig. 2. The slurry composed of the magnetic adsorbent and seawater is introduced from the adsorption vessel into the HGMS through valves V_3, V_5, V_9, V_8, and V_7 after the uranium adsorption process is completed. The HGMS is comprised of an iron yoke with a magnetic coil and a packed filter in the gap of the yoke. The filter bed is composed of a nickel mesh filter (100 mesh) at 86% void volume. The nickel mesh filter is magnetized by the external magnetic field. The magnetic adsorbent in the slurry is trapped

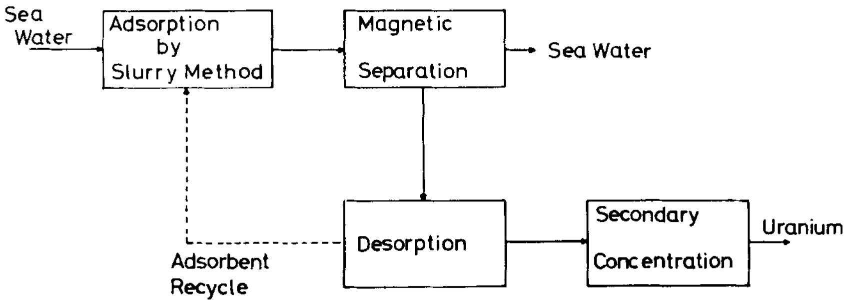

FIGURE 1. Block diagram of uranium extraction by slurry adsorption-magnetic separation.

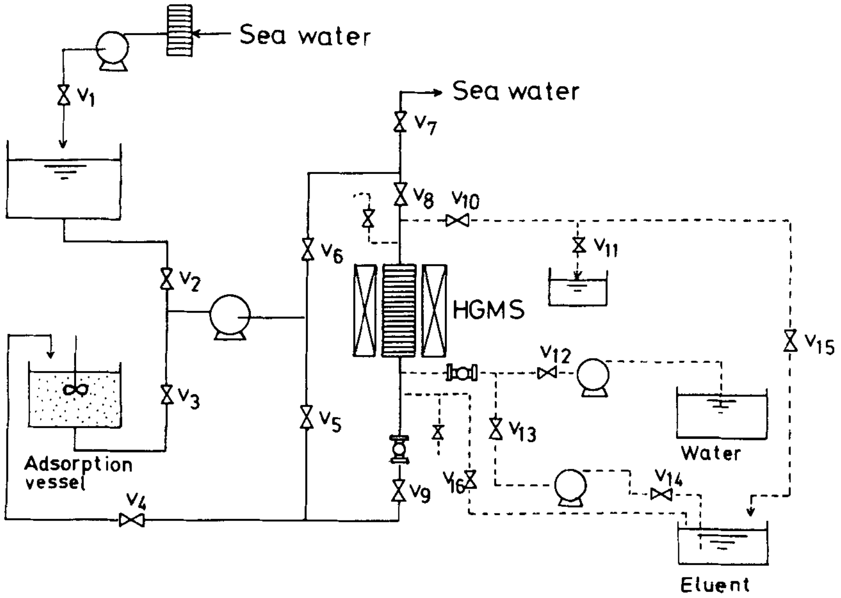

FIGURE 2. Schematic flow diagram of small scale plant.

on the surface of the nickel mesh filter, while seawater passes through the separator. The adsorbent trapped on the filter is then washed with water through valves V_{12}, V_{10}, and V_{11}. Desorption of the uranium adsorbed on the adsorbent is conducted by recycling the eluent through valves V_{14}, V_{13}, V_{10}, and V_{15}. After desorption, the adsorbent is washed with water. When the magnetic field is removed from the mesh, the trapped adsorbent is flushed out of the bed with fresh seawater directly into the adsorption vessel through the operation of valves V_2, V_6, V_8, V_9, and V_4. The magnetic adsorbent and the eluent are used repeatedly in this manner.

MAGNETIC ADSORBENT

Preparation

The magnetic adsorbent, a composite of hydrous titanium and iron oxides, was prepared using a coprecipitaton technique. Urea was added to a solution of titanium sulfate and ferrous sulfate. The solution was stirred for 5-6 h at 95°C to decompose the urea. The precipitate was then filtered, washed with water, and dried at room temperature. The dried sample was crushed and sieved, and a portion of 400-600 mesh selected for use.

The magnetic adsorbent thus prepared was composed of titanium and iron at 2.8 Ti/Fe atom ratio.

Uranium adsorption

The adsorption isotherm for the extraction of uranium from seawater with the magnetic adsorbent is shown in Fig. 3. It was observed that the uranium adsorption from seawater could be described by a Freundlich-type isotherm.

The uranium uptake was found to be about 200 μg per g adsorbent at the normal concentration of uranium in seawater (~3 ppb).

The recovery of uranium from seawater as a function of time at various concentrations of adsorbent is presented graphically in Fig. 4. Uranium recovery increased with concentration of the adsorbent. At adsorbent concentrations above 300 ppm, adsorption equilibrium was attained within 1 h.

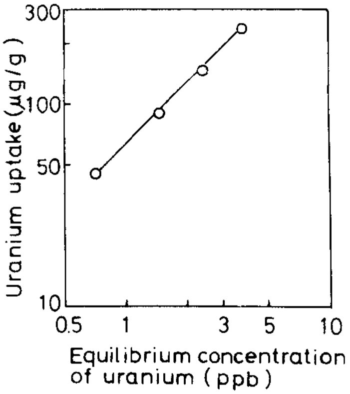

FIGURE 3. Adsorption isotherm of uranium (25°C).

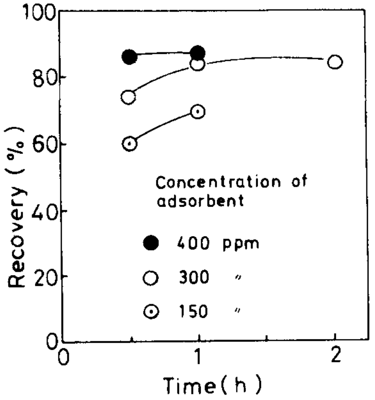

FIGURE 4. Variation of uranium recovery with time.

An adsorption concentration of 400 ppm and a time of 0.5 h were chosen for the pilot test.

Desorption of uranium

Desorption of the uranium adsorbed on the magnetic adsorbent was accomplished using 40 liters of an eluent containing 0.5 mol/L $NaHCO_3$ and 0.5 mol/L Na_2CO_3 at 50°C. For this purpose, 365 g adsorbent, containing 30 μg U per g adsorbent was employed. The

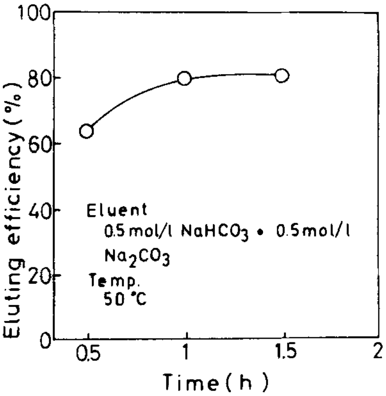

FIGURE 5. Variation of eluting efficiency with time.

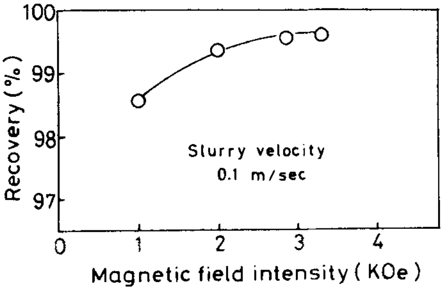

FIGURE 6. Effect of external magnetic field intensity on recovery of adsorbent.

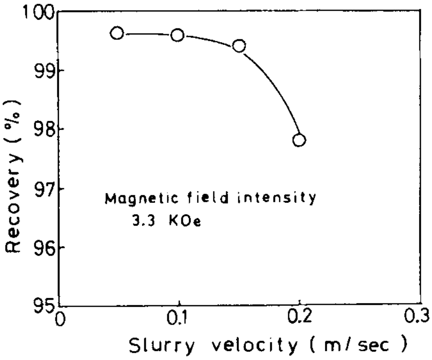

FIGURE 7. Effect of slurry velocity on recovery of adsorbent.

eluent was recycled at a flow rate of 1 m^3/h through the adsorbent trapped on the filter bed of the HGMS. The variation of eluting efficiency with time is presented in Fig. 5. The eluting efficiency was found to be 80% within 1 h.

Magnetic properties

X-ray diffraction measurements indicated that the composite magnetic adsorbent was composed of anatase ($TiO_2 \cdot H_2O$) and magnetite (Fe_3O_4). The uranium adsorption capacity depends mainly on the hydrous titanium oxide, whereas the magnetic separation depends upon the magnetite in the adsorbent.

The magnetic adsorbent used in the experiments was ferromagnetic; the saturated magnetization was about 5 emu/g. An experiment on the recovery of adsorbent from seawater was conducted using the HGMS. The adsorbent-seawater slurry was passed through the packed filter bed (30 cm length and 300 cm^2 cross sectional area) on the HGMS. Recovery of the adsorbent was determined by measuring the titanium content in the slurry before and after magnetic separation. The effect of external magnetic field intensity on the recovery of the magnetic adsorbent is shown in Fig. 6; recovery increases with external magnetic field intensity. It was also observed that recoveries greater than 99% were obtained at magnetic field intensities greater than 2 KOe.

The effect of slurry velocity on the recovery of the magnetic adsorbent is depicted in Fig. 7. Greater than 99% recovery was obtained at slurry velocities less than 0.15 m/sec. Based upon these results, an external magnetic field intensity of 3.3 KOe and a slurry velocity of 0.1 m/sec were chosen in the pilot test.

Extraction of Uranium from Seawater

A sequential program of the extraction process which was conducted using the small scale plant is shown in Fig. 8. Approximately 0.9 m^3 of seawater, containing 400 ppm of adsorbent, was introduced into the adsorption vessel at a flow rate of 25 m^3/h. After the first uranium adsorption (0.5 h), the slurry was passed through the HGMS at a velocity of 0.1 m/sec. Next, the external

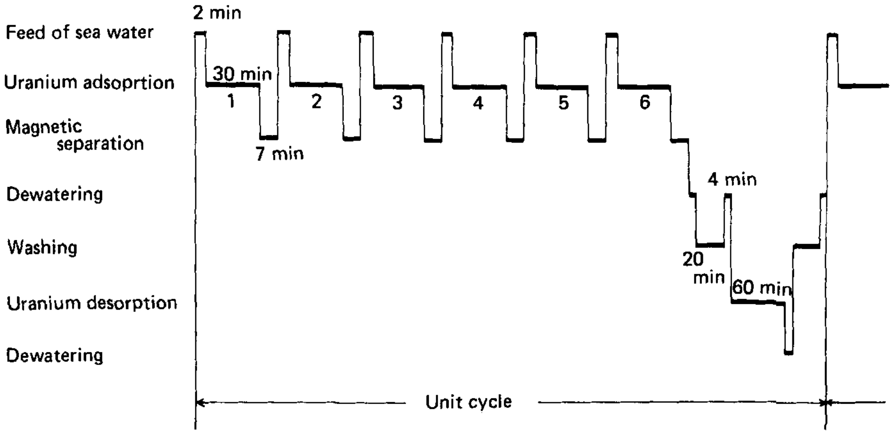

FIGURE 8. Sequential program of extraction process.

magnetic force was removed and the trapped adsorbent flushed from the filter bed into the adsorption vessel with 0.9 m^3 of fresh seawater at a flow rate of 25 m^3/h. The second uranium adsorption process was then started. This sequence was repeated six times. After the adsorption process, the desorption process was conducted over a 1 h period by recycling 40 liters of eluent at 50°C to the adsorbent that was trapped in the HGMS. A unit cycle was comprised of six adsorption processes and one desorption process.

The variation of uranium concentration in the eluent with the number of desorption cycles is presented in Fig. 9. The concentration of uranium in the eluent increased almost linearly in the 1st-3rd cycles. However, the increase in the uranium concentration gradually declined, and no additional desorption occurred during the 7th and 8th cycles. After the 8th cycle of the desorption process using No. 1 eluent, the adsorbent was processed again by a new eluent (No. 2). The uranium continued to be eluted by using the new eluent. Similar curves were obtained with the No. 2 and 3 eluents. It was also noted that a uranium concentration exceeding 1 ppm was not attained.

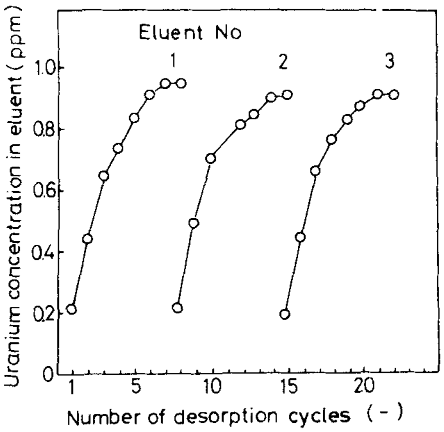

FIGURE 9. Variation of uranium concentration in eluent with number of desorption cycles.

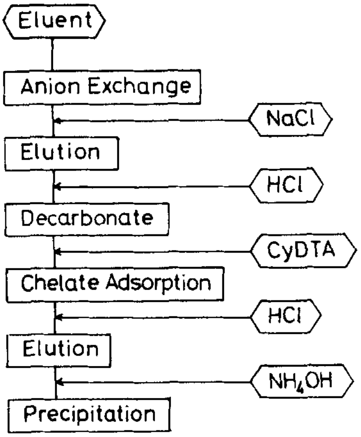

FIGURE 10. Schematic flow diagram of secondary concentration.

From a fundamental study of the desorption process, a distribution coefficient (K_d) of uranium in $NaHCO_3$-Na_2CO_3 solution was found to be 1.2 ($K_d = C_l/C_s$, where C_l is the uranium concentration in the solution in μg/cc and C_s the concentration on the adsorbent in μg/g). C_l is calculated to be 36 ppm when C_s is 30 μg/g at equilibrium. Thus the experimental value obtained in the test is extremely low compared wtih the calculated value. Reasons for the discrepancy are not clear at the present time, but one cause may be an increase in organic materials in the eluent. However, the effect of organic compounds on uranium desorption remains to be investigated.

Secondary concentration and purification of the eluent was performed using the method shown schematically in Fig. 10. The procedure consisted mainly of two steps, anion exchange and chelate adsorption.

As a result, a solution containing uranium at 1,300 ppm was obtained. Finally, aqueous ammonia was added to the solution and a yellow cake of uranium was obtained.

In the uranium extraction experiment, seventy-three cycles of the adsorption-desorption process were performed. The recovery of uranium in the adsorption-desorption process was found to be 42%, and in the secondary concentration process, 88%.

In all, 314 mg of uranium (408 mg as ammonium diuranate) were extracted from 292 m^3 of seawater. The overall recovery of uranium was 37%.

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