

(51) International Patent Classification:
C22B 60/02 (2006.01)(21) International Application Number:
PCT/US2014/013106(22) International Filing Date:
27 January 2014 (27.01.2014)

(25) Filing Language: English

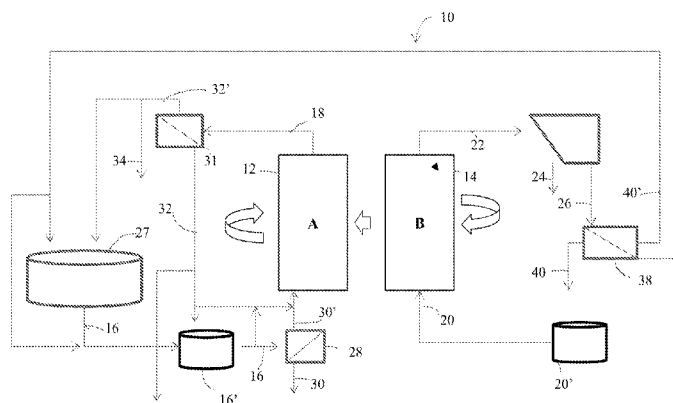
(26) Publication Language: English

(30) Priority Data:
61/767,286 21 February 2013 (21.02.2013) US(71) Applicants: **ROHM AND HAAS COMPANY** [US/US];
100 Independence Mall West, Philadelphia, PA 19106
(US). **DOW GLOBAL TECHNOLOGIES LLC**
[US/US]; 2040 Dow Center, Midland, MI 48674 (US).(72) Inventors: **REZKALLAH, Areski**; 50 Rue Fairdherbe, F-
59260 Lezennes (FR). **AERTS, Peter E.M.**; Ir Ielystraat
21, NL-4561 MH Hulst (NL). **KRUEGER, Robert T.**;
13122 Long Common Parkway, Huntersville, NC 28078
(US).(74) Agent: **BLACK, Edward W.**; The Dow Chemical Com-
pany, Intellectual Property, P. O. Box 1967, Midland,
Michigan 48641-1967 (US).(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).**Published:**

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))

(54) Title: CONTINUOUS ION EXCHANGE PROCESS INTEGRATED WITH MEMBRANE SEPARATION FOR RECOVER-
ING URANIUM

Fig 1



(57) **Abstract:** A continuous ion exchange system and method for recovering uranium from a pregnant liquor solution wherein the method includes the steps of: (a) treating the pregnant liquor solution (16) with a membrane (28) to produce: i) a leach permeate solution (30) at least partially depleted of uranium and carbonate and ii) a leach concentrate solution (30') having a relatively higher concentration of uranium and carbonate and which is at least partially depleted of chloride; (b) passing the leach concentrate stream (30') through an ion exchange bed to load uranium onto a strong base anion exchange resin and produce an untreated barren (18) solution depleted of uranium, (c) passing an eluant solution (20) comprising bicarbonate through the loaded ion exchange bed to strip uranium from the strong base anion exchange resin and produce an eluate (22) comprising uranium and bicarbonate, (d) precipitating uranium (24) from the eluate (22) to produce a residual eluant solution (26) depleted of uranium, and (e) repeating steps (a)-(d).

CONTINUOUS ION EXCHANGE PROCESS INTEGRATED WITH MEMBRANE SEPARATION FOR RECOVERING URANIUM

5 FIELD

The present invention is directed toward a continuous ion exchange process for recovering uranium from pregnant liquor solutions.

INTRODUCTION

10 Continuous ion exchange (CIX) processes have been used since the 1970's to recover uranium from pregnant liquor solutions (PLS). A brief overview of the process is described by: Anton R. Hendriksz and Ronald R. McGregor, "The extraction of uranium from in-situ leach solutions using NIMCIX ion exchange contactor," Annual Uranium Seminar (proceedings) 1980, 4th, pages 121-124. In general, the CIX process involves the use a uranium recovery circuit
15 including of a plurality of ion exchange beds, commonly arranged in carousal, which repetitively cycle through individual process zones including uranium loading and elution. Various anions (e.g. chloride, sulfate, carbonate, bicarbonate) present in the PLS can also absorb on resin exchange sites during the resin loading phase of the process. The extent to which these anions ultimately compete with uranium anions is influenced by their relative concentration and affinity for the resin along with
20 the pH and temperature of the leach solution. The recycling of barren or residual eluant exacerbates this problem by effectively concentrating these competing anions to the point where they result in a loss of separation efficiency, e.g. lower resin capacity, more frequent resin elution, eluant replacement, dilution of PLS, and the like.

25 SUMMARY

The present invention includes a continuous ion exchange system and method for recovering uranium from a pregnant liquor solution that integrates the use of one or more membrane separations to reduce the concentration of competing anions. In one embodiment, the method includes recovering uranium from an alkaline pregnant liquor solution including uranium, carbonate
30 and chloride. The pregnant liquor solution is passed through a plurality of ion exchange beds (12, 14) resin that cycle through process zones as part of a repeating uranium recovery circuit. The method includes the steps of: (a) treating the pregnant liquor solution (16) with a membrane (28) to produce: i) a leach permeate solution (30) at least partially depleted of uranium and carbonate and ii) a leach concentrate solution (30') having a relatively higher concentration of uranium and carbonate
35 and which is at least partially depleted of chloride; (b) passing the leach concentrate stream (30') through an ion exchange bed to load uranium onto a strong base anion exchange resin and produce an untreated barren (18) solution depleted of uranium, (c) passing an eluant solution (20) comprising

bicarbonate through the loaded ion exchange bed to strip uranium from the strong base anion exchange resin and produce an eluate (22) comprising uranium and bicarbonate, (d) precipitating uranium (24) from the eluate (22) to produce a residual eluant solution (26) depleted of uranium, and (e) repeating steps (a)-(d).

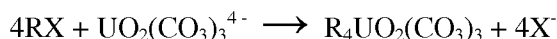
5

BRIEF DESCRIPTION OF THE DRAWINGS

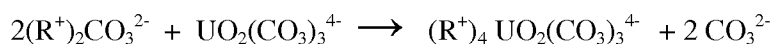
Figure 1 is a schematic view of an embodiment of the present continuous exchange system.

DETAILED DESCRIPTION

10 The invention includes a system and method for recovering uranium from a pregnant liquor solution, ("PLS"). The source of the PLS is not particularly limited but is typically produced by heap leaching, in-situ leaching, vat leaching or pressure leaching of carbonate-containing uranium ores. In one embodiment, the leach ores reside in a lixiviation tank from which the PLS is drawn. The PLS comprises an alkaline solution preferably having a pH of at least 9 and more preferably at
15 least 10; and further includes uranium, bicarbonate, carbonate, sulfate and chloride anions along with their counter cations and corresponding salts. Even though the concentration of these anions is dynamic, they are preferably maintained within the following ranges: carbonate: 10-60 g/L; bicarbonate: 1-20 g/L; chloride: 0 to 10g/L; sulfate: 0-25 g/L. While the tetravalent uranyl tricarbonate complex anion $\text{UO}_2(\text{CO}_3)_3^{4-}$ predominates, a divalent ion $\text{UO}_2(\text{CO}_3)_2^{2-} \cdot 2\text{H}_2\text{O}$ may
20 exist at low carbonate concentration. During the loading phase of the process, the mobile exchange ion ("X," e.g. chloride, hydroxyl, etc.) initially adsorbed on the exchange resin (R) and the uranium anions in solution will proceed as follows:



When an anion exchange resin is provided in the carbonate form, the loading reactions proceeds as
25 follows:



During the elution phase, an eluant solution (e.g. from 50g/L to saturated aqueous bicarbonate solution) is passed through the uranium loaded ion exchange bed and exchanges eluant anions for uranium anions.

30 As part of the present method, the PLS is subject to continuous ion exchange (CIX) including the step of passing PLS through a plurality of ion exchange beds containing strong base anion exchange resin. The beds pass through individual process zones as part of a repeating uranium recovery circuit schematically illustrated in Figure 1. More specifically, a CIX unit is generally shown at 10 including a plurality of ion exchange beds (12, 14) containing a strong base anion

exchange resin that sequentially pass through individual process zones (e.g. A, B) as part of a uranium recovery circuit. Each zone preferably includes at least one ion exchange bed or column, and in practice may include a plurality of individual beds. The method includes the following sequential steps:

5 (a) passing the PLS (16) through an ion exchange bed (zone A) to load uranium onto the ion exchange resin and produce an untreated barren solution (18) which is depleted of uranium, and (b) passing an eluant solution (20) through the uranium loaded ion exchange bed(s) (zone B) to strip uranium from the ion exchange resin and produce an eluate (22). The eluate (22) may be then treated to precipitate out uranium (24) leaving a residual eluate solution (26) that may
10 be optionally reused. The method may include additional process zones as is well known in the art, e.g. rinsing, washing, scrubbing, etc. Processed uranium ore may be stored in a lixiviation tank (27) from which PLS is drawn. PLS and eluant may be maintained in tanks (16'), (20'), respectively. The tanks are in selective fluid communication with the ion exchange beds (12, 14). Fluid flow may be controlled by a plurality of valves and a control panel (not shown) as the beds (12, 14) cycle
15 through the individual process zones (A and B). CIX equipment for performing the subject method is available from PuriTech (e.g. IONEX™), Ionex Separations and Calgon Carbon (e.g. ISEPT™) and is also described in US 7594951. Suitable ion exchange resins include AMBERSEP™ 400 strong base anion exchange resin available from The Dow Chemical Company. This resin includes a styrene-divinylbenzene copolymer (gel) matrix with functional quaternary ammonium groups.
20 The resin may be initially provided in various ionic forms, e.g. sulfate, carbonate, hydroxyl and chloride.

In order to reduce the concentration of competing anions (e.g. chloride) present in the PLS (16), at least a portion of the PLS is be treated with a membrane (28) to produce: i) a leach permeate solution (30) at least partially depleted of uranium and carbonate and ii) a leach concentrate solution
25 (30') having a relatively higher concentration of uranium and carbonate and that is at least partially depleted in monovalent anions (e.g. chloride) as compared with the untreated PLS (16). The leach permeate solution (30) may be disposed or reused. For example, the leach permeate solution (30) may be subject to further membrane treatment (not shown), e.g. with a reverse osmosis membrane (e.g. FILMTEC™ XLE-440). The concentrate solution resulting from such a reverse osmosis
30 treatment includes most of the remaining ionic species (e.g. chloride, sulfate) and can be disposed; whereas the permeate solution can be recycled and used in the lixiviation tank (27) to replace evaporative loss, used to make fresh bicarbonate solution added to the lixiviation tank (27), or used to dilute the PLS (16) or leach concentrate solution (30').

The leach concentrate solution (30') (and optional blended PLS (16)) is passed through an
35 ion exchange bed (12) to load uranium onto the strong base anion resin and produce an untreated

barren solution (18) depleted of uranium. The untreated barren solution (18) may be disposed of, recycled back to the lixiviation tank (27), or in a preferred embodiment, subject to further treatment with a membrane (31). For example, all or a portion of the untreated barren solution (18) may be treated with a membrane (31) to produce: i) a barren permeate solution (32) at least partially
5 depleted of carbonate (and other anions optionally including sulphate and chloride) and ii) a barren concentrate solution (32') having a relatively higher concentration of carbonate. The barren permeate solution (32) may be optionally recycled to (i.e. combined with) the PLS (16) or leach concentrate solution (30') for use in the loading phase of the process. The barren concentrate solution (32') may be optionally disposed (34) or recycled, e.g. all or a portion may be recycled to
10 the lixiviation tank (27). In a preferred embodiment, the barren concentrate solution (32') is subject to further membrane treatment (not shown), e.g. with a reverse osmosis membrane with the resulting permeate being used in the lixiviation tank (27) to replace evaporative loss, used to make fresh bicarbonate solution added to the lixiviation tank (27), or used to dilute the PLS (16) or leach concentrate solution (30').

15 The eluant solution (20) passes through the uranium loaded ion exchange bed(s) (zone B) to strip uranium from the ion exchange resin and produce an eluate (22). The eluate (22) may be then treated to precipitate out uranium (24) leaving a residual eluate solution (26). By way of example, the eluate may be neutralized with sulfuric acid and uranium can be precipitated with hydrogen peroxide. In this example, the resulting residual eluate solution (26) includes sodium sulfate along
20 with carbonate/bicarbonate. This residual eluate solution (26) may then be disposed of, recycled to the lixiviation tank (27) or preferably subject to further membrane treatment. For example, at least a portion of the residual eluate solution (26) may be treated with a membrane (38) to produce: i) a residual eluate permeate solution (40) at least partially depleted of bicarbonate (and uranium) and ii) a residual eluate concentrate solution (42) having a relatively higher concentration of bicarbonate
25 (and uranium) than the residual eluate solution (26). The residual eluate concentrate solution (42) can be recycled directly to the lixiviation tank (27) the PLS (16) or the leach concentrate solution (30'). The residual eluate permeate solution (40) may be disposed, or further treated with membranes (not shown). For example, the residual eluate permeate solution (40) may be further treated with a reverse osmosis membrane (e.g. FILMTEC™ XLE-440 or FILMTEC™ BW30
30 XFR-400/34i or FILMTEC™ XFRLE-400/34i available from The Dow Chemical Company. This treatment creates a second permeate solution that is depleted of almost all ions (e.g. over 98% rejection of chloride) and a second concentrate solution including most of the ions and salts that were present in the residual eluate permeate solution (40). This second permeate solution can be recycled to the lixiviation tank (27), used to prepare fresh bicarbonate solution for addition to the

lixiviation tank (27) or for diluting the PLS (16) or leach concentrate solution (30'). The second concentrate solution can be disposed.

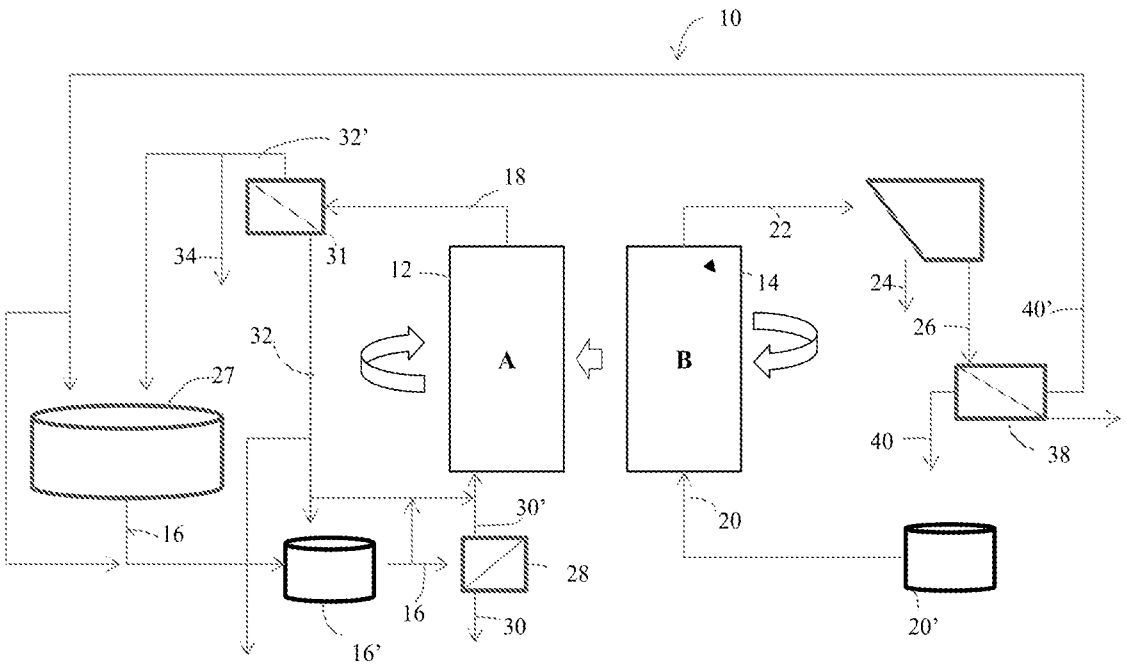
Different membranes may be used depending upon the degree of ion separation desired. Applicable membranes (28, 31 and 38) include nanofiltration and reverse osmosis elements such as
5 FILMTEC™ NF90 and NF 270, FILMTEC™ XLE-440 or FILMTEC™ BW30 XFR-400/34i or
FILMTEC™ XFRLE-400/34i available from The Dow Chemical Company.

Many embodiments of the invention have been described and in some instances certain embodiments, selections, ranges, constituents, or other features have been characterized as being
“preferred.” Characterizations of “preferred” features should in no way be interpreted as deeming
10 such features as being required, essential or critical to the invention. Stated ranges include end
points. The entire subject matter of each of the aforementioned patent documents is incorporated
herein by reference.

CLAIMS:

1. A method for recovering uranium from an alkaline pregnant liquor solution comprising uranium, carbonate and chloride, by passing the pregnant liquor solution through a plurality of ion exchange beds (12, 14) containing strong base anion exchange resin that cycle through process zones as part of a repeating uranium recovery circuit, wherein the method comprises the steps of:
- 5 (a) treating the pregnant liquor solution (16) with a membrane (28) to produce: i) a leach permeate solution (30) at least partially depleted of uranium and carbonate and ii) a leach concentrate solution (30') having a relatively higher concentration of uranium and carbonate and which is at least partially depleted of chloride;
- 10 (b) passing the leach concentrate stream (30') through an ion exchange bed to load uranium onto the ion exchange resin and produce an untreated barren (18) solution depleted of uranium,
- (c) passing an eluant solution (20) comprising bicarbonate through the loaded ion exchange bed to strip uranium from the ion exchange resin and produce an eluate
- 15 (22) comprising uranium and bicarbonate,
- (d) precipitating uranium (24) from the eluate (22) to produce a residual eluant solution (26) depleted of uranium, and
- (e) repeating steps (a)-(d).
2. The method of claim 1 including the steps of:
- 20 (f) treating a portion of the untreated barren solution (18) of step (b) with a membrane (31) to produce:
- i) a barren permeate solution (32) at least partially depleted of carbonate and
- ii) a barren concentrate solution (32') having a relatively higher concentration of carbonate, and
- 25 (g) combining the barren permeate solution (32) with at least one of the pregnant liquor solution (16) or the leach leach concentrate solution (30') of step (a).
3. The method of claim 1 including the steps of:
- (h) treating a portion of the residual eluant solution (26) of step (d) with a membrane (38) to produce:
- 30 i) a residual eluate permeate solution (40) at least partially depleted of bicarbonate and
- ii) a residual eluate concentrate solution (40') having a relatively higher concentration of bicarbonate than the residual eluate solution (26), and
- (i) combining the residual eluate concentrate solution (40') with at least one of the
- 35 pregnant liquor solution (16) or the leach concentrate solution (30') of step (a).

Fig 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/013106

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22B60/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/132138 A1 (BASSIL ANDREW [ZA]) 27 October 2011 (2011-10-27) fig. 1a, 1b, 2-4; p. 5-11 -----	1-3
A	US 4 316 800 A (STANA REGIS R ET AL) 23 February 1982 (1982-02-23) the whole document -----	1-3
A	US 4 410 497 A (OTTO JR JOHN B [US]) 18 October 1983 (1983-10-18) the whole document -----	1-3
A	US 4 312 838 A (YAN TSOUNG-YUAN) 26 January 1982 (1982-01-26) the whole document -----	1-3
	-/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 July 2014

Date of mailing of the international search report

05/08/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Radeck, Stephanie

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/013106

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Emmanuel J. ZAGANIARIS: "Ion Exchange Resins in Uranium Hydrometallurgy", 1 May 2009 (2009-05-01), Books on Demand GmbH, Paris, XP002727545, ISBN: 9782810601882 p. 83-91; p. 110-116; p. 135-147 -----	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/013106

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011132138 A1	27-10-2011	AU 2011243991 B2 CA 2796325 A1 EA 201201438 A1 US 2013039823 A1 WO 2011132138 A1	10-10-2013 27-10-2011 30-04-2013 14-02-2013 27-10-2011
US 4316800 A	23-02-1982	AU 540097 B2 AU 5563080 A CA 1140865 A1 ES 8103185 A1 FR 2449729 A1 OA 6475 A US 4316800 A ZA 8000702 A	01-11-1984 28-08-1980 08-02-1983 16-05-1981 19-09-1980 31-07-1981 23-02-1982 26-08-1981
US 4410497 A	18-10-1983	AU 554585 B2 AU 1021483 A CA 1213149 A1 US 4410497 A	28-08-1986 04-08-1983 28-10-1986 18-10-1983
US 4312838 A	26-01-1982	NONE	