



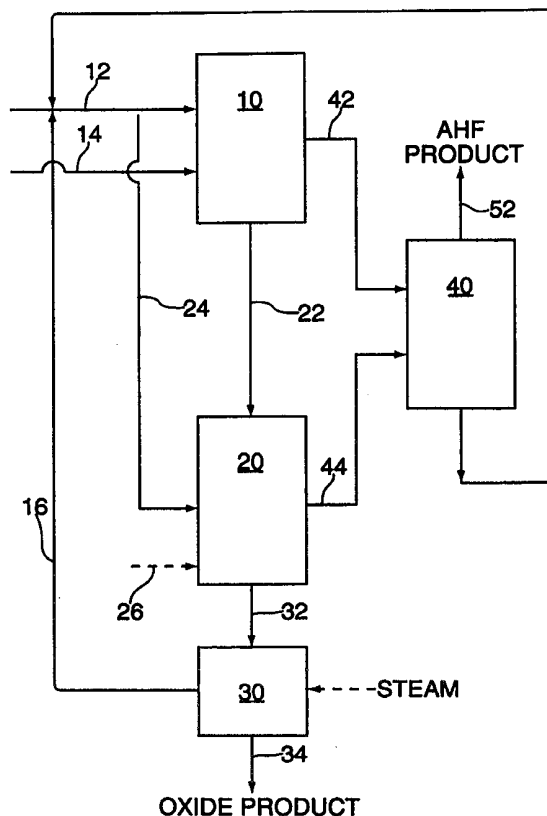
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(21) International Application Number: PCT/US99/01044 (22) International Filing Date: 18 January 1999 (18.01.99) (30) Priority Data: 09/008,123 16 January 1998 (16.01.98) US (71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (72) Inventors: HAGE, Daniel; 775 Highland Church Road, Paducah, KY 42001 (US). MERKEL, Daniel, Christopher; 64 Glenmar Drive, West Seneca, NY 14224 (US). HULSEY, Felton; 212 Baker Drive, Metropolis, IL 62960 (US). (74) Agents: CRISS, Roger, H. et al.; AlliedSignal Inc., Law Dept. (R. Fels), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published Without international search report and to be republished upon receipt of that report.

(54) Title: IMPROVED PROCESS FOR RECOVERING ANHYDROUS HYDROGEN FLUORIDE (AHF) FROM URANIUM HEXAFLUORIDE (UF₆)

(57) Abstract

The invention relates to a two-stage method for recovering products; anhydrous hydrogen fluoride and uranium oxides, particularly triuranium octoxide, from the defluorination of uranium hexafluoride and similar feedstocks which involves treating uranium oxide hydrate intermediate in the second stage (reaction zone) with HF/water azeotrope and/or hydrogen.



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5 **IMPROVED PROCESS FOR RECOVERING ANHYDROUS HYDROGEN
 FLUORIDE (AHF) FROM URANIUM HEXAFLUORIDE (UF₆)**

 The present invention relates generally to a method for recovering useful
products from the defluorination of uranium hexafluoride in a two-stage process where
water/hydrogen fluoride azeotrope and/or hydrogen is fed to the reaction that converts
10 uranyl fluoride to uranyl oxide. More particularly, the present invention relates to a
process for the recovery of commercial grade liquid anhydrous hydrogen fluoride and
water insoluble stable triuranium octoxide, preferably having a low soluble fluoride
content, from uranium hexafluoride.

15 **BACKGROUND OF THE INVENTION**

 Commercially useful uranium isotopes such as U²³⁵ have been produced in well
known processes for over 40 years. The feed material for those processes have been
produced from a uranium hexafluoride (UF₆) enrichment process which takes natural
uranium, which typically contains 0.7% U²³⁵, to suitable levels for nuclear fuel. The
20 enrichment process leaves behind a UF₆ material that contains mostly U²³⁸ and 0.1 -
0.3%U²³⁵. This material is sometimes referred to as depleted UF₆ (DUF₆) and as of yet
has little commercial value although there is hope in the future that new enrichment
technologies will allow for more of the U²³⁵ to be removed from the DUF₆ essentially
turning it into a resource.

25 Much of the DUF₆ that has been produced for the last 40 years is stored in
carbon steel cylinders and amounts to around 50,000 cylinders or over 1 billion pounds
of material. Storage of those cylinders is not considered a long term solution because
of the potential for corrosion of the cylinders which could cause a release of toxic
30 materials into the environment. UF₆ reacts readily with the moisture in the air to form
hydrofluoric acid and water-soluble uranyl fluoride (UO₂F₂). Consequently, DUF₆ is
looked upon as a potential safety and environmental hazard. It is therefore desirable to
provide an effective process which can convert UF₆ into a more stable form, e.g.,
uranium octoxide (U₃O₈). In addition, the process should create virtually no waste
35 while recovering the hydrogen fluoride (HF) values of the UF₆.

While others may have practiced chemical reactions similar to those of the present invention, (U.S. Patent 5,346,684) no one has achieved the objectives of the present invention in the manner in which those objectives are achieved by the present invention. The present invention provides an efficient process for improved recovery
5 of commercially useful anhydrous hydrogen fluoride (AHF) from uranium hexafluoride (UF_6). Furthermore the process of the present invention can also improve production of stable insoluble uranium oxides that contain little soluble fluoride, that is less toxic than UF_6 and can be stored more safely for future use, disposed of in a low radiation level burial site at reduced cost, or used in current shielding applications. While the
10 method in U.S. Patent 5,346,684 may appear similar in some respects to the present invention, the present invention does not employ feed steam for converting uranyl fluoride to uranyl oxide product in the second stage reaction. Yet another process for producing anhydrous hydrogen fluoride is disclosed in the assignee's presently pending U.S. patent application serial no. 08/657,556 filed June 4, 1996.

15

U.S. Patent No. 3,765,844 describes a fluidized bed process for making uranium dioxide by hydrolysis of uranium hexafluoride in a bed of UO_2F_2 particles at temperatures in the range of 500 °C to 900 °C to produce an uranyl fluoride powder which is then subjected to at least two separate pyrohydrolysis treatments in fluidized
20 beds with gaseous mixtures of hydrogen and steam to produce uranium dioxide. Additional fluidized bed processes are described in U.S. Patents Nos. 3,906,081 and 3,978,194.

25

SUMMARY OF THE INVENTION

The present invention provides an improved method for recovering two distinct and separable products from the defluorination of uranium hexafluoride. The first product is a commercial grade liquid anhydrous hydrogen fluoride (AHF). The second is water insoluble uranium oxide such as uranium dioxide (UO_2), uranium trioxide
30 (UO_3) and preferably, stable triuranium octoxide (U_3O_8) which can be stored safely for

future use or disposed of in a conventional manner. Uranium oxides produced by this process preferably have a low soluble fluoride content.

More particularly, the present invention provides an improved method for
5 recovering anhydrous hydrogen fluoride from uranium hexafluoride comprising the steps of (a) in a first reaction zone reacting gaseous uranium hexafluoride with a gaseous azeotrope of hydrogen fluoride and water to produce a uranyl fluoride intermediate and a first mixture comprised of hydrogen fluoride and water; (b) in a second reaction zone reacting said uranyl fluoride intermediate with at least one gas
10 selected from the group consisting of hydrogen fluoride/water azeotrope and hydrogen, to produce uranium oxide and a second mixture comprised of hydrogen fluoride, water and oxygen; (c) separating anhydrous hydrogen fluoride from at least one of said first and second mixtures; (d) separating an azeotrope of hydrogen fluoride and water from at least one of said first and second mixtures; and (e) recycling said
15 azeotrope from step (d) to at least one of said first and second reaction zones.

Preferably, the first and second mixtures are combined before separating either the anhydrous hydrogen fluoride or recycling the azeotrope to a reaction zone. It is also preferred that the separation steps (c) and (d) be effected by conventional
20 distillation.

The uranium oxide products may be recovered from the second reaction zone and treated to remove residual fluorides and other impurities, e.g., by stripping. The first and second reaction zones may be combined in a multi-zone reactor, e.g., a
25 two-zone reactor including both the first and second reaction zones or a three-zone reactor further including a separation/distillation zone could be employed also.

The apparatus for practicing the method may include a first reactor in which a stream of gaseous azeotrope of hydrogen fluoride and water circulates and a second

reactor in which UO_2F_2 is reacted with gaseous hydrogen fluoride azeotrope and/or hydrogen.

5 A gaseous stream of uranium hexafluoride (UF_6) feed is introduced into the circulating azeotrope in the first reactor. The UF_6 reacts with water in the circulating azeotrope stream producing a uranyl fluoride intermediate, e.g., UO_2F_2 , and a first gaseous mixture of hydrogen fluoride and water. As the water is reacted away HF is evolved and the resulting solution becomes enriched with HF.

10 Preferably, the uranyl fluoride intermediate is fed directly, to a second pyrohydrolysis reactor, or a second such zone, and reacted with, either or both of, water/ hydrogen fluoride azeotrope or hydrogen (H_2), to produce uranium oxide products, such as triuranium octoxide, and a second gaseous mixture of water, hydrogen fluoride, and oxygen. The second gaseous mixture may be combined with
15 the first gaseous mixture of water and hydrogen fluoride from the first reactor, condensed and subsequently fed into a separator, e.g., a conventional distillation column. The components of the combined mixtures are separated in the distillation column to obtain a commercial grade anhydrous hydrogen fluoride product stream as overhead and an azeotropic recycle stream containing water and hydrogen fluoride.
20 The azeotropic recycle stream can be used as a feed source for, either or both of, the first and second reactors. The azeotropic recycle stream may be returned in-whole or in-part to the first reactor as feed source for water to the system. The azeotropic recycle stream may also be returned in-whole or in-part to the second reactor as a feed source for water.

25

In the process of the invention hydrogen gas may be used in place of or with the hydrogen fluoride/water azeotrope to feed to the second reactor. The resulting product stream of hydrogen fluoride and hydrogen gas (in small amounts) comprises a second mixture that can be combined with the hydrogen fluoride rich first mixture
30 from the first reactor, condensed and fed to a separator, e.g., a conventional distillation column to recover anhydrous HF.

A third reactor for separating soluble fluorine and other volatile impurities in the uranium oxide products, e.g., a stripper, may be added. Solid triuranium octoxide product may be fed to the stripper and contacted with steam. If a third reactor is required any make-up water that is needed for the entire system may be fed to it. The
5 resulting mixture of steam with a small amount of HF may be combined with HF and vaporized to provide HF/water azeotrope feed for the first and/or second reactor.

BRIEF DESCRIPTION OF THE DRAWING

10 Figure 1 is a schematic flowchart of the method of the present invention.

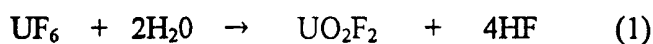
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

With reference to Fig. 1, the units of operation include a first reactor 10, a second reactor 20, a fluorine stripper 30 and a separation unit 40 (distillation column).
15 The material streams defined by the method are designated and are further described with reference thereto. A water/hydrogen fluoride azeotrope stream 12 comprised of about 37-38% hydrogen fluoride is introduced to first reactor 10. The azeotrope maybe initially heated by an external source (not shown) and may be comprised of recycle from downstream steps in the method. In the first reactor 10 the actual
20 temperature depends on various process parameters and is usually in the range of about 550 to about 700°C (about 1000 to about 1300°F), and more preferably about 600 to about 650°C (about 1100 to about 1200°F). First reactor 10 is preferably operated at a pressure in the range of about -1 psig to about + 1 psig. Pressures less than atmospheric are most preferred.

25

UF₆ feed stream 14, comprised of gaseous uranium hexafluoride (UF₆), is fed into the first reactor 10 and contacts stream 12 therein. The UF₆ reacts with some of the water in stream 12 to produce a uranyl fluoride intermediate (e.g., UO₂F₂) and HF in accordance with the following generalized equation (1):

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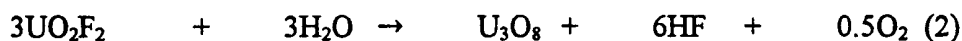


As the reaction of UF_6 with the azeotrope proceeds the HF and UO_2F_2 content of the mixture increases.

5 The first reactor 10 has two outlet streams 22 and 42 which are recovered separately. Stream 22 comprised of UO_2F_2 is fed into second reactor or zone 20 where it reacts with the hydrogen fluoride, water azeotrope stream 24, and/or hydrogen gas 26. Second reactor 20 is preferably operated at a pressure in the range of about -1 psig to about + 1 psig. Pressures less than atmospheric are most
10 preferred. The second reactor 20 is preferably operated at a temperature of about 480 to about 760°C (about 900 to about 1400°F) and more preferably about 600 to about 650°C (about 1100 to about 1200°F).

The reaction in second reactor 20 follows the generalized equation (2):

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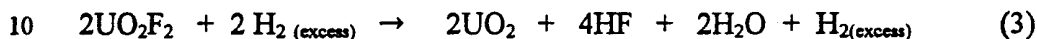


As indicated by equation (2), outlet stream 32 may comprise triuranium
20 octoxide (U_3O_8) product with small amounts of soluble (unreacted) fluoride and outlet stream 44 comprises a gaseous mixture of water, HF, and oxygen.

The reaction products of the azeotrope and uranyl fluoride intermediate leave second reactor 20 separately as bottom stream 32 and overhead stream 44. Stream 32
25 is fed to a fluorine stripper 30, if purification, e.g., removal of soluble fluorides is desired. Stripper 30 is heated with steam feed 31 or in another conventional manner. Two separate outlet streams, 16 (steam/HF) and 34 (oxide product), leave fluoride stripper 30. Oxide product stream 34 may comprise triuranium octoxide and/or other products, and less than about 20 ppm preferably less than about 10 ppm soluble
30 fluoride and may be easily recovered from the process for storage or disposal. Stream 16, comprised of essentially steam and HF, can be converted to azeotrope by adding

HF and then used as a feed stream for first and/or second reactors 10 and 20. When stream 32 is substantially free of soluble fluoride, fluorine stripper 30 may not be necessary.

- 5 In an alternative embodiment stream 22 may be reacted in second reactor 20 with hydrogen gas instead of or in addition to HF/water azeotrope. In this embodiment stream 26 comprises hydrogen. Here the second reactor's 20 outlet streams 32 and 44 are characterized by the generalized equation (3):



First reactor 10 and second reactor 20 outlet streams 42 and 44, when combined, comprise a gaseous mixture of HF/water, possibly oxygen and in some cases H₂.

15

Separation unit 40 may be a distillation column wherein streams 42 and 44 are combined and thereafter separated into two separate streams 52 and 54.

- Stream 52 is a gaseous mixture of HF, possibly oxygen, and essentially free of water and uranium. Outlet stream 52 can be fed subsequently to a condenser 50 and
 20 separated into a gaseous stream 58 comprised essentially of oxygen, which can be vented to a scrubber (not shown) and a separate liquid stream 56 composed of commercial grade anhydrous hydrogen fluoride with less than about 1 ppm uranium and less than about 500 ppm water. Outlet stream 54 from column 40 is a liquid stream typically comprised of about 37% HF and about 63% water which is the azeotrope
 25 composition of HF/water and may be used in its entirety or in-part as recycle feed to first reactor 10 and/or second reactor 20.

The following examples demonstrate the practice and utility of the present invention, but are not to be construed as limiting the scope thereof.

30

EXAMPLE 1

A simple test reactor is constructed from 1.5 inch MONEL pipe and an adjustable muffle-type heater so that the temperature inside the pipe can be adjusted to the desired range. The opening at one end of the pipe is provided with a gas-feed inlet and the opposing end is provided with an gas outlet fitted with an appropriate scrubber device, e.g., KOH absorbers.

Boats, i.e., sample holders, that fit within the reactor are also fashioned from MONEL.

In a reactor as described above, Samples 1 and 2 are converted to U_3O_8 by direct reaction at a temperature of $649^{\circ}C$ ($1200^{\circ}F$) with HF/water azeotrope fed through the reactor inlet. The flow rate of HF/water azeotrope to Sample 1 is 1.5 grams per minute and to Sample 2 is 0.8 grams per minute. The residence times (time in the reactor under reaction conditions) for Samples 1 and 2 are 15 minutes and 30 minutes, respectively. Thereafter, the Samples are weighed and stored in a desiccator.

TABLE 1

	Initial Wt. grams	Initial % Soluble Fluoride	Final Wt. grams	Final % Soluble Fluoride	% Conversion
Sample 1	4.00	12.2	3.80	5.3	56.8
Sample 2	4.06	12.2	3.72	1.6	87.0

The conversions of 56.8 % and 87 % demonstrate that the reaction of uranyl fluoride and HF azeotrope under the stated conditions is effective and commercially feasible.

Sample 2 indicates that longer residence times are desirable. Conversion was calculated as follows:

$$\frac{\text{Initial \% Soluble Fluoride} - \text{Final \% Soluble Fluoride}}{\text{Initial \% Soluble Fluoride}} \times 100$$

EXAMPLE 2

In a reactor as described above two additional samples 3 and 4 of UO_2F_2 are reacted at a flow rate of 1 gm/min at about 760°C (1400°F) with HF azeotrope for about two hours. The samples are arranged in the reactor for more even temperature distribution. Thereafter, the samples are desiccated and weighed.

TABLE 2

	Initial Wt. grams	Final Wt. grams	% Conversion
Sample 3	5.93	5.29	99.7
Sample 4	5.27	4.71	99.8

The soluble fluoride in samples 3 and 4 is 310 and 220 ppm, respectively.

EXAMPLE 3

In this experiment UO_2F_2 is reacted with H_2 at 649°C (1200°F) for 30 minutes substantially in accordance with Example 1 and the results are shown in Table 3 below.

TABLE 3

	Initial Wt. grams	Final Wt. grams	% Conversion	F %
Sample 5	4.01	3.52	94.6	0.65

The conversion of 94.6 % demonstrates that UO_2F_2 can be reacted with H_2 under the stated conditions successfully.

5

EXAMPLE 4

This experiment demonstrates the effectiveness of fluorine stripper 30 for removing residual soluble fluoride from stream 32. A sample 6 of pyrohydrolyzed U_3O_8 containing 164.8 ppm F was heated for 30 minutes using steam with the results shown in Table 4 below.

10

TABLE 4

	Initial ppm F	Initial Wt. grams	Final Wt. grams	F ppm
Sample 6	165	3.54	3.51	26

While the particular process for recovery of anhydrous hydrogen fluoride and uranium oxide products from depleted, natural or enriched uranium hexafluoride as herein shown and disclosed in detail is fully capable of obtaining the objects and providing the advantages herein before stated, it is to be understood that it is merely illustrative of the presently preferred embodiments of the invention and that no limitations are intended to the details of operation herein shown other than as described in the appended claims.

15

20

WHAT IS CLAIMED IS:

1. A method for recovering anhydrous hydrogen fluoride from uranium hexafluoride comprising the steps of:
 - 5 (a) in a first reaction zone reacting gaseous uranium hexafluoride by contact with a gaseous azeotrope of hydrogen fluoride and water to produce an uranyl fluoride intermediate, and a first gaseous mixture comprised of hydrogen fluoride and water;
 - (b) reacting said uranyl fluoride intermediate with at least one of hydrogen
10 gas and a gaseous azeotrope of water and hydrogen fluoride in a second reaction zone to produce a second mixture comprised of water, hydrogen fluoride oxygen, and uranium oxide products;
 - (c) separating anhydrous hydrogen fluoride from at least one of said first and second gaseous mixtures; and
 - 15 (d) optionally separating an azeotrope of hydrogen fluoride and water from at least one of said first and second gaseous mixtures; and,
 - (e) recycling said azeotrope to at least one of said first and second reaction zones.
- 20 2. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, further comprising the step of:
 - (f) recycling said liquid stream of hydrogen fluoride and water azeotrope
25 to said first reactor.
3. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 2, further comprising the step of:
 - (g) recycling a part of said liquid stream of HF and water azeotrope to said
30 second reactor in place of or as a supplement to said gaseous water feed.

4. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, wherein said hydrogen fluoride/water azeotrope feed to the second reaction zone comprises about 37 weight % to about 63 weight % HF.

5

5. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, wherein said first reactor is operated at a pressure of about - 1 psig to about +1 psig.

10

6. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, wherein said first reactor is operated at a temperature of about 550 to about 700°C.

15

7. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, wherein said temperature in said second reactor ranges from about 480 to about 760°C.

20

8. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, wherein said temperature in said second reactor preferably ranges from about 600 to about 650°C.

25

9. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, wherein said second reactor is operated at a pressure of about - 1 to about + 1 psig.

10. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, further comprising the step of separating soluble fluorine and other impurities from the uranium oxide product in a third reactor operated at a pressure less than about + 1 psig.

30

11. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, wherein said uranium oxide product is triuranium octoxide.

5 12. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, wherein said uranium oxide product is uranium trioxide or uranium dioxide.

10 13. A method for recovering anhydrous hydrogen fluoride and a uranium oxide product from uranium hexafluoride as stated in claim 1, where said uranium hexafluoride is supplied from depleted, natural, or enriched uranium hexafluoride.

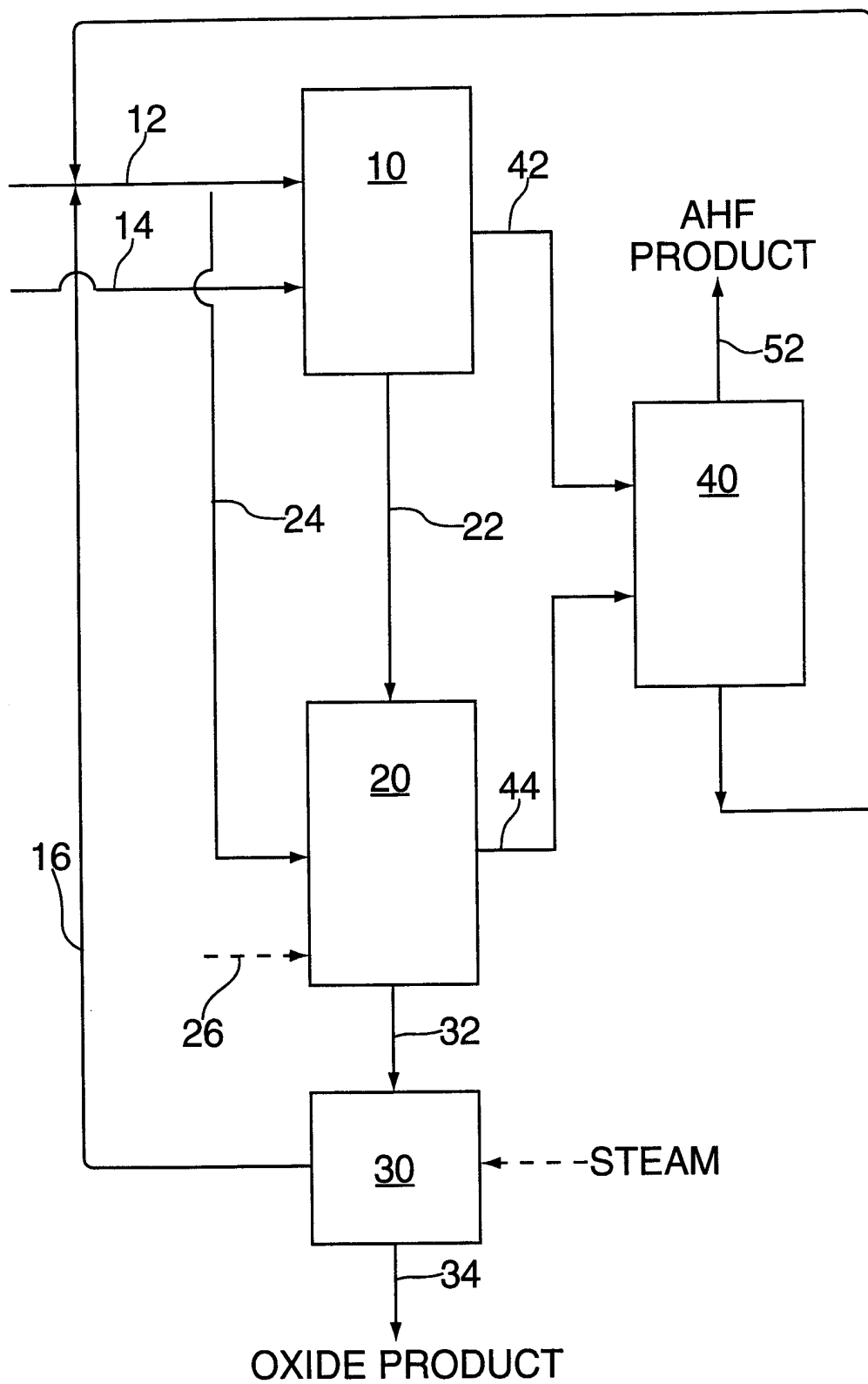


FIG. 1