PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : C01B 7/00	A1	(11) International Publication Number: WO 87/ 00157
		(43) International Publication Date: 15 January 1987 (15.01.87)

(21) International Application Number: PCT/US86/01294

(22) International Filing Date: 13 June 1986 (13.06.86)

(31) Priority Application Number: 748,294

(32) Priority Date: 24 June 1985 (24.06.85)

(33) Priority Country: US

(71) Applicant: ALUMINUM COMPANY OF AMERICA [US/US]; 1501 Alcoa Building, Mellon Square, Pittsburgh, PA 15219 (US).

(72) Inventors: LOUTFY, Raouf, O. ; 4660 N. Via Madre, Tucson, AZ 85749 (US). YOUNG, Suzanne ; 444 W. Orange Grove Road, Tucson, AZ 85704 (US). WITHERS, James, C. ; 3770 Larrea Lane, Tucson, AZ 85749 (US).

(74) Agents: SULLIVAN, Daniel, A., Jr. et al.; Aluminum Company of America, Patent Division, Alcoa Center, PA 15069 (US).

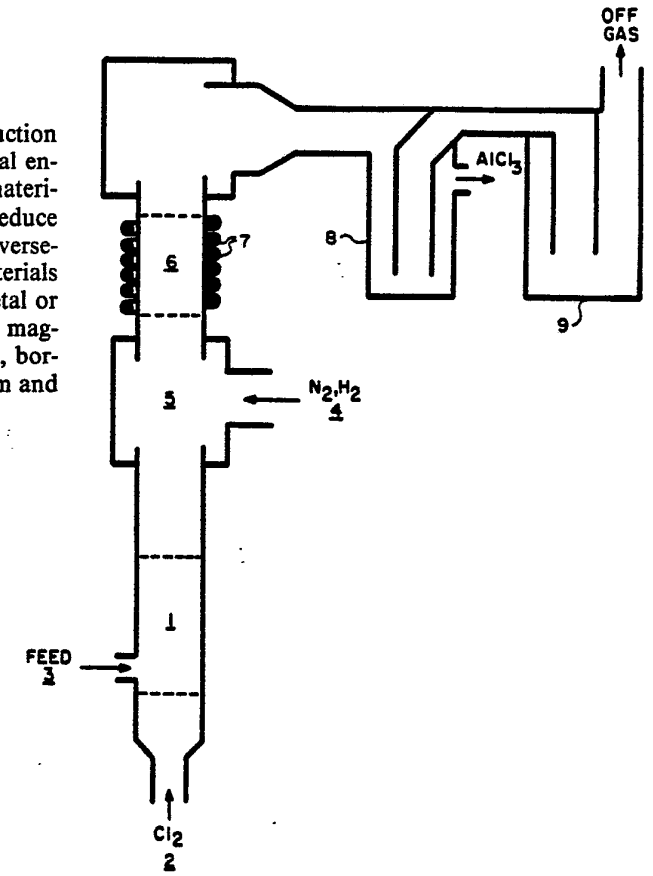
(81) Designated States: AU, BR, DE (European patent), FR (European patent), JP, NO.

Published
With international search report.

(54) Title: REDUCTION OF ORGANOHALOGEN COMPOUNDS IN METAL AND METALLOID CHLORIDE PRODUCTION STREAMS

(57) Abstract

Gaseous metal or metalloid chloride production streams (1) are subjected to the application of thermal energy in the presence of hydrogen or a surface active material (6) for a time and at a temperature sufficient to reduce the organohalogen compounds but not materially adversely affecting the chloride. Suitable surface active materials include coke, activated carbon and alumina. The metal or metalloid may be for instance, aluminium, titanium, magnesium, molbydenum, tungsten, tantalum, beryllium, boron, zirconium, hafnium, niobium, or silicon. Titanium and magnesium, and especially aluminum, are preferred.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GA**	Gabon	**MR**	Mauritania
AU	Australia	**GB**	United Kingdom	**MW**	Malawi
BB	Barbados	**HU**	Hungary	**NL**	Netherlands
BE	Belgium	**IT**	Italy	**NO**	Norway
BG	Bulgaria	**JP**	Japan	**RO**	Romania
BR	Brazil	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SN**	Senegal
CH	Switzerland	**LI**	Liechtenstein	**SU**	Soviet Union
CM	Cameroon	**LK**	Sri Lanka	**TD**	Chad
DE	Germany, Federal Republic of	**LU**	Luxembourg	**TG**	Togo
DK	Denmark	**MC**	Monaco	**US**	United States of America
FI	Finland	**MG**	Madagascar		
FR	France	**ML**	Mali		

REDUCTION OF ORGANOHALOGEN COMPOUNDS IN METAL AND METALLOID CHLORIDE PRODUCTION STREAMS

Technical Field

The invention herein relates to the production of metal and metalloid chlorides from their oxides. More particularly it relates to a method of purifying the chloride product stream of undersirable impurities from the chlorination reaction.

Background Art

It is known that metals and metalloids can be produced by reduction of their chlorides, and that the chlorides themselves can be produced by the chlorination of various metal and metalloid compounds, notably the metal oxides or oxide-containing compositions. Typical of the metals which can be so produced are titanium from $TiCl_4$ reacted from titania, and magnesium from $MgCl_2$ reacted from magnesia. One of the most important processes commercially is the production of aluminum metal by reduction of aluminum chloride, $AlCl_3$. The aluminum chloride itself may be produced by reductive chlorination of alumina or aluminous oxides with chlorine in the presence of a carbonaceous reductant. The chemistry of this reaction is well known, having been described in numerous publications including U.S. Patent No. 3,760,066.

For brevity, most of the remainder of this disclosure will be in terms of the aluminum reactions. It will, however, be recognized that the process herein is equally applicable to analogous chlorination processes involving

compounds of metal and metalloids such as titanium, magnesium, molybdenum, tungsten, tantalum, beryllium, boron, zirconium, hafnium, niobium and silicon (as indicated in U.S. Patent No. 4,459,274.)

It has been recognized that the aluminum chloride production process yields not only the desired aluminum chloride but also a variety of byproducts and unreacted raw materials. For instance, U.S. Patent No. 3,786,135 describes the gaseous products of the reaction as including aluminum chloride, carbon oxides and entrained solid and liquid particles including aluminum, carbon, aluminum oxychloride and/or aluminum hydroxychloride as well as condensable volatile constituents. Various processes have been proposed for elimination or reduction for these unwanted byproducts; for instance, the aforesaid U.S. Patent No. 3,786,135 describes a process involving multi-stage selective cooling to separate the gaseous aluminum chloride product from the unwanted gaseous components. A similar process is described in U.S. Patent No. 3,929,975.

It has also been recognized that among the gaseous products of the reductive chlorination process are a number of different halogenated organic compounds which are formed by the reaction of the chlorine and the carbonaceous reductant (which will hereinafter often be referred to as "carbon" for brevity). Prominent among these byproduct organohalogen compounds are the polychlorinated biphenyls (PCBs) which have in recent years been identified as carcinogenic. Because of the hazardous and/or polluting nature of the PCBs and many of the other organohalogens, it

is important that the level of such compounds in the product aluminum chloride stream be substantially reduced or virtually eliminated if possible, either by destruction of the compounds or chemical conversion to nonhazardous materials.

In other contexts a variety of reactions have been described for converting or destroying organohalogen compounds. For instance, in U.S. Patent No. 4,351,978 a process is described in which PCBs are reacted with hydrogen in the presence of a hydrogenation catalyst, such as a Raney nickel catalyst, to form hydrocarbons or halohydrocarbons. Similarly, in U.S. Patent No. 2,886,605 a process is described in which polyhalogenated hydrocarbons are converted to halohydrocarbons of lower halogen content or to hydrocarbons by reaction with hydrogen in the presence of a catalyst consisting essentially of cuprous halide impregnated in porous active alumina. The same patent also describes as prior art reactions in which the organohalogen compounds are reacted with steam or hydrogen over a catalyst comprising titanium oxide or tin oxide impregnated with copper chloride. U.S. Patent No. 4,144,152 describes a process in which organohalogen compounds are dehalogenated by being subjected to ultraviolet radiation and hydrogen in the absence of any substantial amount of oxidizing agent. This patent also describes a preferred system in which the organohalogen compounds are treated with ultraviolet radiation and hydrogen in an alkaline solution.

While these various reactions to degrade or destroy organohalogen compounds have been known, none is applicable to treatment of the product stream of the aluminum chloride production process. This is because the various prior art processes utilize reactants and/or reaction conditions in which the desired gaseous aluminum chloride product would also be degraded or destroyed. Since the aluminum chloride is to be used as a raw material for the production of metallic aluminum on an industrial scale, it would therefore be of interest to have a process which would permit the amount of undesirable organohalogen compounds in the aluminum chloride product stream to be substantially lessened and/or virtually eliminated without detrimental effect to the aluminum chloride product.

Disclosure of the Invention

We have now invented a process for the reduction of gaseous organohalogen compounds in a gaseous stream also containing gaseous metal or metalloid chlorides, such as aluminum chloride, without significant degradation of the desired product chlorides. The process comprises subjecting the gaseous stream to the application of thermal energy in the presence of hydrogen or a surface active material, or both, for a time and at a temperature sufficient to reduce the organohalogen compounds but not materially adversely affect the metal or metalloid chlorides.

Preferred surface active materials include the solid feed material itself which is to be chlorinated, similar oxides or carbonaceous materials, which may if desired be activated. The surface active material must also be such

that it is either inert toward the hydrogen, metal chloride and chlorine, or, if reactive, such that any product formed will not contaminate the chloride product.

Depending on the particular embodiment of the invention used herein, the organohalogen content in the product chloride stream may be reduced by from 50 percent to 99.8 percent or better.

Description of the Drawing

The single Figure of the drawing is a schematic representation of one embodiment of an apparatus for performing the present invention.

Modes for Carrying Out the Invention

As described above, the invention herein involves subjecting the gaseous product stream from the reaction in which a metal or metalloid chloride (exemplified by aluminum chloride) is produced by reductively chlorinating the corresponding oxide (or a mixture containing the oxide) with a carbonaceous reductant (e.g., carbon) and chlorine, to the application of thermal energy in the presence of hydrogen or a surface active material, or both, for a time and at a temperature sufficient to reduce or substantially eliminate the organohalogen content of the stream without materially affecting the desired gaseous chloride product. Because this basic process can be operated in several different embodiments, it will be recognized that somewhat different,

but often overlapping, reaction conditions will apply depending on the particular embodiment being considered. Those skilled in the art, however, having before them the descriptions and examples to be set forth below, will find no difficulty in making the routine determinations of the optimum reaction conditions to be utilized in any particular embodiment of the invention.

As noted above, this disclosure is primarily in terms of aluminum reactions. The process herein is equally applicable to analogous chlorination processes involving compounds of metal and metalloids such as titanium, magnesium, molybdenum, tungsten, tantalum, beryllium, boron, zirconium, hafnium, niobium and silicon as indicated in U.S. Patent No. 4,459,274.

There are various forms of thermal energy which may be used in this process to initiate and promote the reduction reactions, including microwave and radio frequency (RF) energy. These latter forms, however, require relatively high temperature environments to produce economically feasible reaction rates. They also use specialized equipment which is not normally found in chemical plants and which adversely effects the economics of the process. The thermal energy may also be supplied to the reaction by infrared radiant heaters, gas-fired reactors or other known types of thermal energy generators through which the gaseous product stream may be passed or in which it may be contained.

The application of thermal energy to the gaseous product stream in this process must be done in the presence of hydrogen, a surface active material, or both. It is known that application of thermal energy alone will decompose organohalogen compounds if the temperature is high enough, i.e., on the order of about 950°C (1740°F). However, it has been found that it is not economical in practice to raise the gaseous aluminum chloride product stream to that temperature level and maintain it there for the necessary time. In addition, such high temperatures require the use of more thermally resistant processing equipment if the equipment is not to be rapidly deteriorated by such temperatures. In the present invention, however, it has been found that good results can be obtained in the temperature range of from ambient temperature up to about 700°-750°C (1290°-1380°F) depending on the particular combination of reaction conditions being used. Preferred within this range are temperatures of from about 200°-650°C (390°-1200°F).

When hydrogen is to be used, it may be present as hydrogen gas, producer gas or a reducing gas such as methane.

When a surface active material is to be present, it must be one which promotes the degradation of the organohalogen compounds. However, it must not attack the hydrogen, chlorine or metal or metalloid chloride product present. It may be inert to these components, or, if reactive with any component, it must not produce any reaction product which attacks, degrades or contaminates the chloride. In some

cases the surface active material may be one of the reactants itself, such as alumina in the aluminum chloride process. Other suitable materials include carbonaceous materials such as coke or activated carbon. Among other materials which may suitably be used are compositions which contain oxides in their mixture of components, such as the partially calcined aluminum chloride hexahydrate (PCACH) produced according to the process of co-pending U.S. patent application No. 06/519,795 to R.O. Loutfy and J.C. Withers, which has been published as International Publication No. WO85/00800 (February 28, 1985) under the Patent Cooperation Treaty (US/RO). Cokes may include fully calcined, partially calcined or pretreated petroleum coke. As noted, the materials may be further surface activated, as with activated carbon or activated alumina, by conventional means. Surface areas of the surface active materials may vary widely; satisfactory results have been obtained with coke having a surface area of 1.8 m^2/g, alumina at approximately 80 m^2/g and highly disordered activated carbon at 1400 m^2/g. As will be seen from the Examples below, better results were obtained with the higher surface area materials.

Considerable advantage can often be obtained by using both hydrogen and a surface active material in the present process.

The process herein may be operated in a wide variety of combinations with the aluminum chloride production process. For instance, alumina, coke and chlorine may be reacted in a chlorinator with the product stream containing the gaseous

aluminum chloride and organohalogen compounds then being passed to a decomposer in which the present process is operated using hydrogen and with thermal energy creating a temperature in the range of 200°-650°C (390°-1200°F) in the presence of an activated alumina, carbon or coke. When the surface active material is spent, it is recycled to the chlorinator to serve as a reactant therein. A purified gaseous aluminum chloride stream is recovered from the decomposer.

A typical apparatus used to conduct the process of this invention is shown schematically in the Figure. Fluid bed reactor 1 is either continuously or batch fed with starting materials 3 such as the aforesaid PCACH (an oxide-containing composition) mixed with a coke activated by partial calcination (typically in a weight ratio of 80:20 respectively). Chlorine gas 2 (which may be mixed with nitrogen gas) is fed to the bottom of the reactor 1 to fludize the solid reactants and to chlorinate the PCACH to produce anhydrous aluminum chloride ($AlCl_3$). The $AlCl_3$ produced flows upward to mixing chamber 5 where it is mixed with hydrogen or nitrogen gas 4 or both. The product gas stream also contains all the undesirable chlorinated by-product gases such as PCBs. The mixed gas streams flow into reaction bed 6 containing the surface active material, such as activated alumina or coke or one or more of the reactant materials, such as PCACH. The bed is heated to the desired temperature by heating coils 7. As the gases pass through the bed 6 the chlorinated hydrocarbons are

decomposed to chlorine gas, hydrocarbons, water vapor and/or carbon oxides. The $AlCl_3$ is then recovered in desublimer 8 while the other gases pass through to scrubber 9 where they are separated and the chlorine recovered. This type of apparatus was utilized in the Examples below.

The following Examples will illustrate several embodiments of the present invention.

Example 1

The condensed gaseous products from the production of aluminum chloride by chlorination at 650°C (1200°F) of partially calcined aluminum chloride hexahydrate using partially calcined coke were found to contain an average of 3500 ppm organohalogen compounds. These product streams were subsequently subjected to application of thermal energy in a decomposer at various temperatures, both with and without hydrogen present, and with no surface active material present. The results are presented in Table 1 below.

Table 1

Temperature °C	Temperature °F	Organohalogen Content, ppm Without H	Organohalogen Content, ppm With H
250	480	3500	1220
650	1200	3375	760
750	1380	n.m.	48

(n.m. = not measured)

It will be evident that from the above data the application of heat alone (within the temperature range of this process and below the normal decomposition temperatures of the organohalogen compounds) produces no significant

reduction of the organohalogen compounds. The application of energy without the simultaneous presence of hydrogen will not be expected to produce a significant reduction in organohalogen content until the temperature reaches the decomposition point of the organohalogen compounds, which as noted is approximately 950°C (1740°F).

It will be evident, however, that the use of hydrogen in conjunction with the application of energy produces marked reductions in the amount of organohalogen compounds present leading to reductions of approximately 65%, 75% and 98% respectively.

Example 2

Samples of the same aluminum chloride reaction stream were subjected to application of thermal energy in the presence of a surface active material but without hydrogen present. A control with no surface active material was also used, which is the same as the control of Example 1. Table 2 below illustrates the effects of different surface active materials: reactants PCACH or coke, as described in Example 1, and a high surface area (1400 m^2/gm) commercial activated carbon (Witco Chemical Corp. product "Witco 950").

Table 2

Temperature °C	°F	Organohalogen Content, ppm No Catalyst	PCACH	Coke	Activated Carbon
250	480	3500	863	1900	25
650	1200	3375	602	765	<1

It will be immediately evident from these data that the use of a surface active material, particularly a high

surface area material such as the activated carbon, produces marked reductions in the organohalogen compound content in the product $AlCl_3$ even at low temperatures. With the use of higher temperatures and high surface area catalysts, the organohalogen compounds can be virtually eliminated from aluminum chloride stream.

Example 3

Samples of the same aluminum chloride reaction stream were subjected to application of thermal energy by radiative heating in the presence of different surface active materials and hydrogen. The results are illustrated in Table 3 below.

Table 3

Temperature °C	°F	Organohalogen Content, ppm Alumina	Coke	Alumina/Coke	Activated Carbon
250	480	913	1900	n.m.	<5
650	1200	83	483	295	<1

(n.m. = not measured)

The alumina/coke mixture was the PCACH/coke reaction mixture to a test reactor (as reactor 1 in the Figure). It will be seen by comparison of the data of Tables 1 and 2 with these data that, except at low temperature, the combination of the surface active material and the hydrogen has a synergistic effect, reducing the organohalogen compound content below that obtained with the surface active material or hydrogen alone. It is preferable from an economic point of view to use the chlorination reactor feed (i.e., the alumina/coke mixture) as the surface active

material so as to be able to pass the material to the reactor after it has been spent as a surface active material.

Example 4

A series of experiments was conducted to illustrate temperature and residence time as reaction conditions. Apparatus as illustrated in the Figure was used. The generation of $AlCl_3$ was continuously maintained by feeding PCACH and partially calcined coke in a fluid bed chlorination reactor 1. The temperature of bed 6 was controlled at the various temperatures listed. Residence time was varied by changing the length of bed 6. The results of the experiments using hydrogen alone, with no surface active agent, are illustrated in Table 4. Comparison should be made with the control experiments shown in Table 1.

Table 4

Temperature °C	Temperature °F	Residence Time, sec.	Organohalogen Content, ppm
250	480	6.9	2294
250	480	14.2	1220
650	1200	5.2	924
650	1200	13.4	760
750	1380	13.4	48

These data were curve fitted and the following mathematical model with r^2 of 0.9 was obtained:

$$C_xCl_y = 3345 - 2.75(Temp) - 84.06(RT) \quad (1)$$

where "C_xCl_y" is the organohalogen content in the product $AlCl_3$ (in ppm) after treatment, "Temp" is the Celcius temperature of bed 6 and "RT" is the residence time of the $AlCl_3$ gas in bed 6 in seconds.

Without destruction (i.e., when Temp = 0°C and RT = 0) the content of C_xCl_y is equivalent to the intercept of 3345 ppm. This value agrees well with the typical organohalogen contents observed experimentally for control samples (e.g., those of Example 1). Complete elimination of the organohalogens using hydrogen could theoretically be obtained by varying temperature and residence time in accordance with Equation (1), and in practice significant reductions are obtained in this manner. For instance, at 750°C (1380°F) and a residence time of 15.2 seconds virtual elimination of the organohalogen in the $AlCl_3$ stream should be achieved.

Example 5

The experiments of Example 4 were repeated but with a surface active material present along with the hydrogen. The particular surface active material used was the alumina (PCACH)/coke feed to the system. The results of these experiments are illustrated in Table 5 below.

Table 5

Temperature °C	Temperature °F	Residence Time, sec	Organohalogen Control, ppm
600	1110	2.5	531
600	1110	5.3	426
600	1110	9.0	288
650	1200	2.5	295
650	1200	4.0	230
650	1200	5.4	180
650	1200	7.2	110
700	1290	2.6	37
750	1380	3.3	0

As with the data of Example 4, these data were fitted to a curve having an r^2 of 0.92 and the formula:

$$C_xCl_y = 2800 - 3.7(Temp) - 34.2(RT) \qquad (2)$$

It is apparent that there is a synergistic effect obtained by combining the use of a surface active material and hydrogen to reduce or eliminate organohalogens. For example, at 750°C the total elimination of organohalogens can be accomplished with residence times on the order of only about one second in the presence of both hydrogen and a surface active material (Equation 2; Table 5), while with hydrogen alone approximately 15 seconds are required (Equation 1; Table 4).

It will be understood of course that the curves defined by Equations 1 and 2 are fitted from experimental data and therefore represent statistical approximations of reaction kinetics. Those using these equations (or analogous equations derived from other data samples) can expect that individual runs will yield organohalogen contents which will vary from the values predicted by those equations by increments which themselves are within statistically defined

ranges. All such results are intended to be included within the scope of this invention.

It will also be understood that the variables of hydrogen or surface active material, temperature and residence time can be optimized for each individual system to reach the desired resulting level of organohalogen content in the product $AlCl_3$ stream. Residence time will usually vary within the range of 1 to 20 seconds and temperatures will vary between 250°C and 750°C (480°-1380°F).

As noted above, this invention is also applicable to removing organohalogens from the product streams of the chlorination to other metal chloride products. For example, the production of $MgCl_2$ produces organohalogens according to the reaction:

$$2MgO + 2(x+1)C + (y+2)Cl_2 \longrightarrow 2MgCl_2 + CO_2 + 2C_xCl_y$$

The C_xCl_y content can be controlled as described by application of thermal energy to the product stream in the presence of hydrogen and/or a surface active material (e.g., megnesia, titania or zinconia).

It will be evident from the above that there are many embodiments of this invention which while not specifically described above are clearly within the scope and spirit of the invention. This invention should therefore be considered to be limited only by the appended claims and not by the foregoing description which is intended to be exemplary only.

INDUSTRIAL APPLICABILITY

The invention herein is applicable for reducing organohalogen compound content in a gaseous stream containing a metal or metalloid chloride.

CLAIMS

1. A process for the reduction of gaseous organohalogen compounds in a gaseous stream also containing at least one gaseous metal or metalloid chloride without significant degradation of said chloride, which comprises subjecting said stream, outside of a reactor for producing said chloride, to the application of thermal energy in the presence of hydrogen or a surface active material, or both, for a time and at a temperature sufficient to reduce the organohalogen compounds but not materially adversely affecting said chloride.

2. A process as in claim 1 wherein hydrogen and chlorine are present and there is an absence of copper chloride.

3. A process as in Claim 1 wherein a surface active material is present.

4. A process as in Claim 3 wherein said surface active material is an oxide or a carbonaceous material.

5. A process as in Claim 4 wherein said oxide is one of the feed materials to the chlorination process in which said chloride is produced.

6. A process as in Claim 4 wherein said carbonaceous material is coke or activated carbon.

7. A process as in Claim 1 wherein the temperature is in the range of ambient up to 750°C.

8. A process as in Claim 7 wherein said temperature is in the range of 200°-650°C.

9. A process as in Claim 1 wherein said thermal energy is infrared radiant energy.

10. A process as in Claim 1 wherein said thermal energy is provided by a gas-fired reactor.

11. A process as in Claim 1 wherein said metal or metalloid is aluminum, titanium, magnesium, molybdenum, tungsten, tantalum, beryllium, boron, zirconium, hafnium, niobium and silicon.

12. A process as in Claim 11 wherein said metal is aluminum, titanium or magnesium.

13. A process as in Claim 12 wherein said metal is aluminum.

14. A process as in Claim 5 wherein after said surface active material is spent it is passed as feed to the chlorination process.

15. A process as claimed in claim 2, wherein a surface active material is present together with the hydrogen.

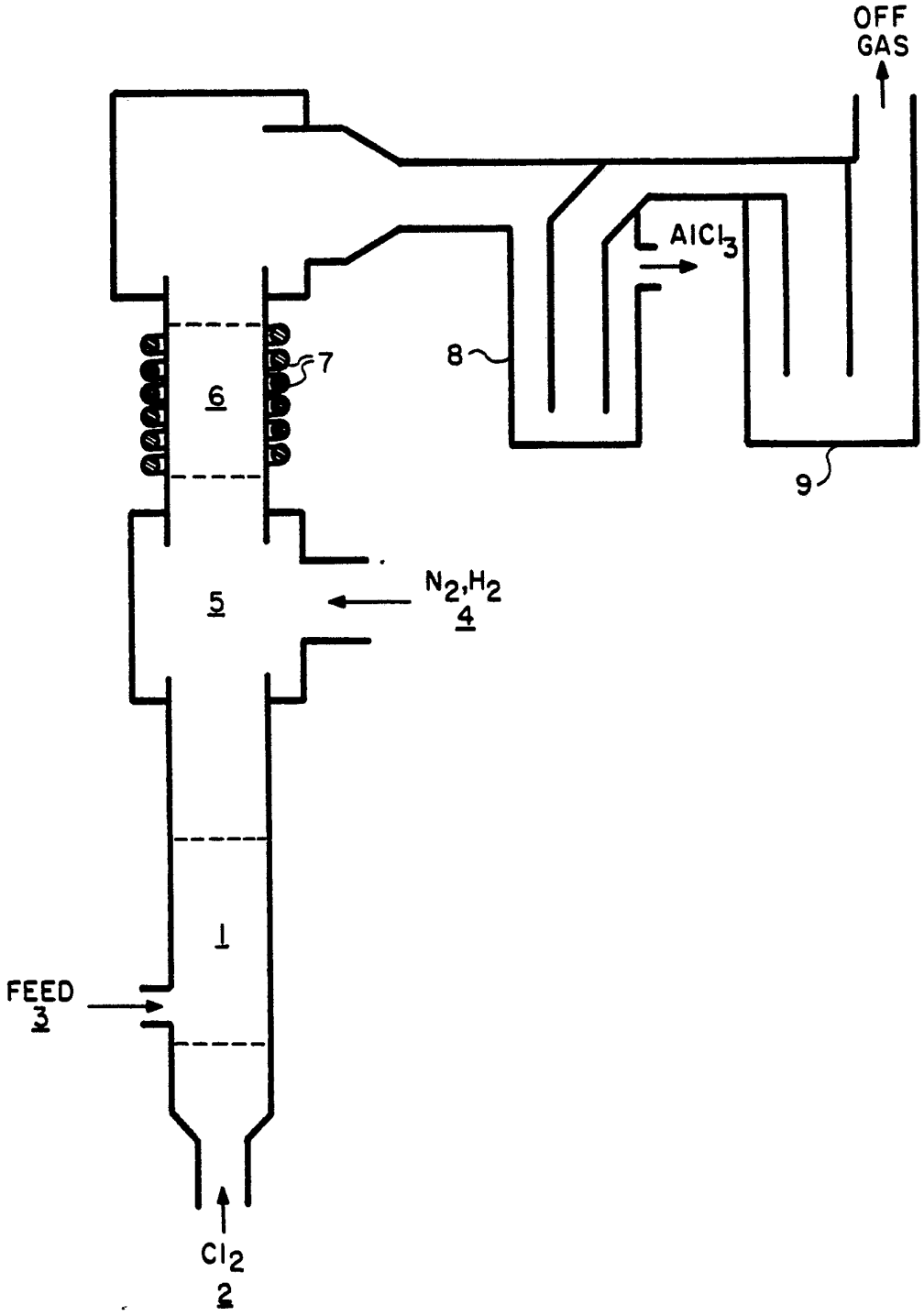
16. A process as claimed in claim 15, said surface active material comprising an oxide and a carbonaceous material.

17. A process as claimed in claim 16, wherein said surface active material comprises feed material to the chlorination process in which said chloride is produced.

18. A process as claimed in claim 17, wherein after said surface active material is spent it is passed as feed to the chlorination process.

19. A process as claimed in claim 18, wherein said surface active material comprises an alumina/coke mixture.

20. A process as claimed in claim 19, wherein the alumina comprises PCACH.


OFF GAS
AlCl3
8
7
6
9
5
N2,H2
4
1
FEED
3
Cl2
2

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01294

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.[4] C01B 7/00

U.S. Cl. 423/240

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	423/137,240,245,495,496

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 4,284,607, (Cuileiton et al.) 18 August 1981, see the entire document.	1 and 3-14
Y	US, A, 4,459,274, (Loutfy et al.) 10 July 1984, see entire document.	2 and 15-18
Y	US, A, 4,351,978, (Hatano et al.) 28 September 1982, see entire document.	2 and 15-18

* Special categories of cited documents: [15]

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

"E" earlier document 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

"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

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
09 July 1986	Lori Freeman 21 JUL 1986
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	Lori Freeman

Form PCT/ISA/210 (second sheet) (May 1986)