A PROCESS OF PRODUCTION OF CONCENTRATED FERRIC CHLORIDE SOLUTION FROM THE WASTE HYDROCHLORIC ACID PICKLE LIQUOR

Fig. 1

A process of production of concentrated ferric chloride solution which used in the waste water treatment processes as a flocculation agent and making use of hydrochloric acid waste pickle liquor which resultant from steel surface treatment processes "pickling". The process is carried out using the hypochlorous acid (HOC1) as an oxidizing agent, hypochlorous acid convert the ferrous chloride (FeCl2) t ferric chloride (FeCl3) and react with the hydrochloric acid (HCl) content to produce chlorine gas (Cl2), the chlorine gas used for further oxidation of ferrous chloride to ferric chloride. The final product of this process is aqueous solution of ferric chloride free of any contaminations (ferrous chloride and hydrochloric acid) within concentration reaches 40 by weight percent.
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A process of Production of concentrated ferric chloride solution from the waste hydrochloric acid pickle liquor.

**Technical Field:**

The present invention relates to a process of converting ferrous chloride to ferric chloride.

It is known that in the processes of steel surface treatment the steel surface treated by a solution of hydrochloric acid in a step called "pickling", the resultant liquor from this step containing ferrous chloride (FeCl₂) is called "waste pickle liquor", the pickle liquor generally contain (01% - 05%) hydrochloric acid and (13% - 25%) ferrous chloride.

**Background Art:**

Several methods have been proposed for economically treating the hydrochloric acid waste pickle liquor by converting it to a useful product like ferric chloride (FeCl₃) to avoid disposal it like that, and avoid the environmental and pollution problems.

One such method is a chlorine oxidation method wherein chlorine reacted with waste pickle liquor which containing ferrous chloride through a vertical reactor, introducing a major amount of chlorine at the base of the reactor, introducing a side stream of ferric chloride solution into the reactor, and recovering an aqueous solution essentially containing ferric chloride from the base of the reactor.

Another method is a reacting of an aqueous solution of ferrous chloride at a temperature above 50°C (132°F) in a contact with oxygen-containing gas which can be air, but preferably oxygen-
enriched air up to 100% oxygen, the pickle liquor entering the reactor is enriched with hydrochloric acid so that the resultant pickle liquor contains a sufficient concentration of (CF) ions to convert all (FeCl₂) to (FeCl₃).

**Disclosure of Invention:**

The present invention aims to provide a method wherein ferrous chloride (FeCl₂) may be converted to ferric chloride (FeCl₃) easily with higher purity than the conventional methods, said method uses little energy and produce ferric chloride solution within concentration reaches 40% by weight, that is by oxidizing the waste hydrochloric acid waste pickle liquor by an oxidizing agent resulting ferric chloride and chlorine gas, the chlorine gas used to carry out extra oxidizing reaction to convert more ferrous chloride to ferric chloride.

The present invention is based on the above findings and comprises the following major points.

1) **Optionally a concentration step:** Wherein the hydrochloric acid waste pickle liquor solution is concentrated by heating and evaporation.

   The heating temperature advantageously ranges from (50 to 100°C), at the atmospheric pressure, the amount of water to be evaporated off depends on the concentration of the ferrous chloride (FeCl₂) in the feed waste pickle liquor and on the desired concentration of the ferric chloride (FeCl₃) in the final product, the resultant vapor contain essentially water and hydrochloric acid (HCl), this vapor pass through a scrubber to collect the hydrochloric acid content, the hydrochloric acid resultant reused again in the pickling processes.
After the waste pickle liquor solution reaches the desired concentration it transferred to the next step.

2) **Chlorine gas oxidation step:** it is the 1st step of the oxidation stage (the oxidation stage contains 2 steps)
At which we utilize the oxidizing characteristics of chlorine gas to convert the ferrous chloride content in the concentrated waste pickle liquor to ferric chloride, that is through a vertical reactor, the chlorine gas introduced from the base of the reactor and the concentrated waste pickle liquor from the top of the reactor, his will give the chance to chlorine gas to oxidize the ferrous chloride and convert it to ferric chloride according to the following reaction formula.

\[
2\text{FeCl}_2(\text{aq}) + \text{Cl}_2(\text{g}) = 2\text{FeCl}_3(\text{aq})
\]

Any process ensures that the chlorine and ferrous chloride are intimately contact to produce ferric chloride could be used here.

The partially conversion of ferrous chloride to ferric chloride in this step depends on the amount of chlorine gas produced from the followed step and the amount of ferrous chloride in the waste pickle liquor.

3) **hypochlorous acid (HOCl) oxidation step:** it is the 2nd step of the oxidation stage (the oxidation stage contains 2 steps)
the resultant solution from the chlorine gas oxidation step contains essentially ferrous chloride which did not oxidized in the last step, ferric chloride that produced from the last step and hydrochloric acid, this solution introduced to a reactor to treated with hypochlorous acid (HOCl), the hypochlorous acid oxidize all the remaining ferrous chloride to ferric chloride, additional it react with the remaining hydrochloric acid and produces chlorine gas (Cl\(_2\)) which oxidize ferrous chloride to ferric chloride and the remaining chlorine gas transferred to the previous step (chlorine gas oxidation step), that is according to the following reaction formulas:
a- Oxidization of ferrous chloride to ferric chloride.

\[ \text{Fe}^{2+} + \text{HOCl} + \text{H}^+ = \text{Fe}^{3+} + \text{HCl} \]

b- Reaction of hypochlorous acid with hydrochloric acid.

\[
\begin{align*}
\text{HOCl} (\text{aq}) + \text{HCl} (\text{aq}) &= \text{Cl}_2 \text{(gas)} + \frac{1}{2} \text{O}_2 \text{(liq)} \\
2\text{FeCl}_2 (\text{aq}) + \text{Cl}_2 \text{(gas)} &= 2\text{FeCl}_3 \text{(liq)}
\end{align*}
\]

This reaction carried out at reactor within room temperature and atmospheric pressure, mixing is preferable to ensure reaction competition and reduce time of the process.

The produced chlorine gas from this process is collected from the reactor via top outlet and transferred to the base of the reactor of the latter process (chlorine gas oxidation process).

According to this method, the produced aqueous solution comprising concentration reaches 40 weight percent of ferric chloride, without any contamination of hydrochloric acid (HCl) or ferrous chloride (FeCl₂).

**Brief description of the drawing:**

The attached drawing is a schematic representation of a preferred embodiment of the invention.

The numbers between brackets refer to the flow streams, while the alone numbers without any brackets refer to the processes.

The present invention comprises: a) Optionally a concentration step, b) Chlorine gas oxidation step, c) Hypochlorous acid (HOCl) oxidation step.

**a) Optionally a concentration step:**

The waste pickle liquor (1) contains aqueous solution with ferrous chloride within ranges of (13% to 25%) by weight and hydrochloric acid concentration within ranges of (01% to 05%) by weight is supplied to the concentration (process no.O1), the heat source which supplied is partially evaporate the said waste pickle liquor, the resultant vapors (2) are
essentially contains water and hydrochloric acid, the said vapors are passed through a scrubber to recover the hydrochloric acid content.

b) **Chlorine gas oxidation step:**

The concentrated waste pickle liquor (3) which resultant from the concentration process (process no.01) is supplied via inlet at the top of the chlorine gas oxidation process (process no.02) reactor, the chlorine gas stream (6) which produced from the hypochlorous acid oxidation process (process no.03) is supplied to the chlorine gas oxidation process (process no.02) through the flow line (6) via inlet at the base of the chlorine gas oxidation process (process no.02) reactor.

c) **Hypochlorous acid (HOCl) oxidation step:**

The resultant aqueous solution (4) which resultant from the chlorine gas oxidation process (process no.02) contains essentially ferrous chloride (FeCl\(_2\)) which did not converted to ferric chloride by chlorine gas, ferric chloride (FeCl\(_3\)) and traces of hydrochloric acid (HCl) is supplied to the hypochlorous acid (HOCl) oxidation process (process no.03) reactor, hypochlorous acid (HOCl) is supplied to the reactor through the flow line (5), as a result from the reaction carried out during the process no.03 the chlorine gas produced and transferred to the chlorine gas oxidation process (process no.02) through the flow line (06), while the concentrated ferric chloride (FeCl\(_3\)) solution produced through the flow line (7).
Claims

1- A method of production of a concentrated ferric chloride solution by using hypochlorous acid (HOC1) to convert ferrous chloride (FeCl₂) which present in waste hydrochloric acid pickle liquor to ferric chloride (FeCl₃) and utilize the oxidation characteristics of chlorine gas which produced through the process for further oxidation of the ferrous chloride to ferric chloride, this said method comprising the following steps:

1) A concentration step: Wherein the hydrochloric acid waste pickle liquor solution is concentrated by heating and evaporation. The heating temperature advantageously ranges from (50 to 100 °C), at the atmospheric pressure, the amount of water to be evaporated off depends on the concentration of the ferrous chloride (FeCl₂) in the feed waste pickle liquor and on the desired concentration of the ferric chloride (FeCl₃) in the final product, the resultant vapor contain essentially water and hydrochloric acid (HCl), this vapor pass through a scrubber to collect the hydrochloric acid content, the hydrochloric acid resultant reused again in the pickling processes. After the waste pickle liquor solution reaches the desired concentration it transferred to the next step.

2) Chlorine gas oxidation step: it is the 1st step of the oxidation stage (the oxidation stage contains 2 steps)
at which we utilize the oxidizing characteristics to convert the ferrous chloride content in the concentrated waste pickle liquor to ferric chloride, that is through a vertical reactor, the chlorine gas introduced from the base of the reactor and the concentrated waste pickle liquor from the top of the reactor, his will give the chance to chlorine gas to oxidize the ferrous chloride and convert it to ferric chloride according to the following reaction formula.

$$2\text{FeCl}_2(\text{liq}) + \text{Cl}_2(\text{gas}) = 2\text{FeCl}_3(\text{liq})$$

Any process ensures that the chlorine and ferrous chloride are intimately contact to produce ferric chloride could be used here.

The partially conversion of ferrous chloride to ferric chloride in this step depends on the amount of chlorine gas produced from the followed step and the amount of ferrous chloride in the waste pickle liquor.

3) **hypochlorous acid (HOC!) oxidation step**: it is the 2nd step of the oxidation stage (the oxidation stage contains 2 steps)

   the resultant solution from the chlorine gas oxidation step contains essentially ferrous chloride which did not oxidized in the last step, ferric chloride that produced from the last step and hydrochloric acid, this solution introduced to a reactor to treated with hypochlorous acid (HOC1), the hypochlorous acid oxidize all the remaining ferrous chloride to ferric chloride, additional it react with the remaining hydrochloric acid and produces chlorine gas (Cl$_2$) which oxidize ferrous chloride to ferric chloride and the remaining chlorine gas transferred to the previous step (chlorine gas oxidation step), that is according to the following reaction formulas:
c- Oxidization of ferrous chloride to ferric chloride.

\[ \text{Fe}^{2+} + \text{HOCl} + \text{H}^+ = \text{Fe}^{3+} + \text{HCl} \]

d- Reaction of hypochlorous acid with hydrochloric acid.

\[
\begin{align*}
\text{HOCl} \text{ (liq)} & + \text{HCl} \text{ (liq)} = \text{Cl}_2 \text{ (g)} + \text{H}_2\text{O} \text{ (liq)} \\
2\text{FeCl}_2 \text{ (liq)} & + \text{Cl}_2 \text{ (g)} = 2\text{FeCl}_3 \text{ (liq)}
\end{align*}
\]

This reaction carried out at reactor within room temperature and atmospheric pressure, mixing is preferable to ensure reaction competition and reduce time of the process.

The produced chlorine gas from this process is collected from the reactor via top outlet and transferred to the base of the reactor of the latter process (chlorine gas oxidation process).

According to this method, the produced aqueous solution comprising concentration reaches 40 weight percent of ferric chloride or any desired concentration needed in the final product, without any contamination of hydrochloric acid (HCl) or ferrous chloride (FeCl\(_2\)).

Characterized in that is no heating energy used through all process steps except the optionally concentration step.

2- A method according to claim 1, characterized in that chlorine gas which produced from the hypochlorous acid oxidation step is utilized in a prior step to convert partial amount of ferrous chloride to ferric chloride.
3- A method according to claim 1, characterized in that the hypochlorous acid used to oxidize all the remained ferric chloride in the waste pickle liquor, ferrous chloride and hydrochloric acid in room temp and atmospheric pressure with mixing.

4- A method according to claim 3, characterized in that no contaminations (ferrous chloride and hydrochloric acid) produces in the ferric chloride solution final product.

5- A method according to claim 3, characterized in that variable concentration of ferric chloride solution final product could be obtained by control the feed waste pickle liquor concentration.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC*: C23G 1/36 (2006.01) ; C01G 49/10 (2006.01)
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)
IPC*: C23G, C01G

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)
WPI, EPODOC; PAJ, STN-Patdp

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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I-0 Further documents are listed in the continuation of Box C.
I-0 See patent family annex.

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Name and mailing address of the ISA/AT
Austrian Patent Office
Dresdner Straße 87, A-1200 Vienna

Facsimile No. +43 / 1 / 534 24 / 535

Authorized officer
STEPANOVSKY M.

Telephone No. +43 / 1 / 534 24 / 135

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